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**Proceedings of the  
twelfth cotton utilization research  
conference held at New Orleans, La.  
May 8-10, 1972**

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## PREFACE

The 12th Cotton Utilization Research Conference was held in New Orleans, La., May 8, 9, and 10, 1972. This Conference is held annually by the Southern Marketing and Nutrition Research Division to report progress made in important areas of cotton research during the year.

Topics discussed included fundamental investigations of cotton cellulose, mechanical processing, and special purpose finishes. Flame retardancy and durable press was emphasized.

This year we were fortunate in being able to include reports by Cotton Incorporated and the International Institute for Cotton on their research and development studies to enhance the utilization of cotton.

These proceedings report in summary or in full the statements presented by the various speakers during the Conference.

C. H. Fisher, Director  
Southern Marketing and Nutrition Research Division

GENERAL CHAIRMAN  
Robert C. Jackson

CONFERENCE COORDINATOR  
Shirley T. Saucier

PROGRAM COMMITTEE  
Bruno H. Wojcik, Chairman  
Wilson A. Reeves  
John D. Guthrie  
Henry L. E. Vix  
Robert T. O'Connor  
Ralph A. Rusca  
Mary E. Carter

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## WELCOME

by

C. H. Fisher, Director  
Southern Marketing and Nutrition Research Division  
New Orleans, La.

It is my privilege, on behalf of the Southern Marketing and Nutrition Research Division (SMNRD) to welcome you to this 12th Cotton Utilization Research Conference. We thank you for attending and participating in this Conference. We are grateful because you have given us the opportunity of reporting promptly on our advances in cotton research. We invite you to ask questions and to offer comments at this Conference and on any occasion.

We disseminate information about our cotton research by various conferences and publications and with the help of the Agricultural Experiment Stations. Several years ago, for example, we held a conference on vapor-phase finishing of cotton to summarize progress in this area.

Miscellaneous Publication #893 by Marie A. Jones contains abstracts of all the cotton research papers published by the Southern Regional Research Laboratory (SRRL) during the first twenty years of its existence.

We are now preparing a supplement to include abstracts of all our cotton publications for the ten-year period ending December 31, 1969. With the publication of this supplement, we shall have a useful summary of the nearly 2,000 cotton research articles published during the first 30 years of the existence of SRRL.

In calendar year 1971, progress in our research was reported in 298 technical papers and 175 presentations to scientific and industrial groups, and in 65 patent applications. Eight patent licenses were granted.

As many of you are aware, we publish semiannually a list of our publications and patents with abstracts. To facilitate progress in cotton research by many organizations, we are initiating the practice of publishing a list of our cotton research articles and patents, with abstracts, on a quarterly basis. This will accelerate the process of disseminating promptly the results of our cotton research. This will be a part of our effort not only to do valuable cotton research, but also to report the results promptly.

I wish to bring to your attention several changes and events of the past year. Two Laboratories formerly associated with SMNRD have been made a part of our sister Southeastern Marketing and Nutrition Research Division, which is headquartered at Athens, Ga. One is the

Fruit and Vegetable Products Laboratory, Winter Haven, Fla., and the other is the Food Fermentation Laboratory, which works in cooperation with the North Carolina State University and Agricultural Experiment Station, Raleigh.

The Textile and Clothing (T&C) Laboratory, Knoxville, Tenn., has been made a part of SMNRD. We are fortunate because Mary E. Carter, a distinguished textile scientist, joined SMNRD as Chief of the T&C Laboratory. The T&C Laboratory is located on the campus of the University of Tennessee, and we are grateful for the privilege of working in cooperation with the University of Tennessee, particularly its Department of Home Economics.

During the past year, our research, conducted in cooperation with many other organizations, continued to be profitable. Some of our research findings have been adopted by other organizations and used for practical purposes. Some of our developments that were previously commercialized are being used more extensively.

Our scientists and engineers have contributed importantly to 15 commercialized developments during the past year. Most of these involve cotton and cottonseed.

New crosslinking chemicals, featuring advantageous "leaving groups" are being used commercially to make durable-press textile products.

The Zirchrome Process for producing sunlight and rot-resistant fabrics for outdoor use has been licensed by four companies.

A major firm has requested and been issued a license to practice the invention under U.S. Patent No. 3,416,880 entitled "Modification of Cellulosic Textiles with Methylolated Hydroxyalkyl Carbamates."

Although a number of flame-retardant formulations containing THPC are used commercially, two new products are now offered by American Cyanamid, their first entry into the THPC area. One of the products, TKC, is a 60 percent solution of THPC. The other product is THP, an adduct of THPC and urea.

The SRRL Fiber Retriever, Model M-2, is being used commercially. This is the first commercial application of the M-2 device, which provided maximum cleaning at slightly increased cost as compared with the simple M-1 model.

The M-1 Retriever is installed on an estimated 18,000 carding machines.

The SRRL Bale-Opener-Blender Patents No. 3,166,797 and 3,458,904 have been licensed to a large corporation that plans to manufacture the Blender for companywide use.

Advances in the measurement and effect of fiber hooks and fiber orientation on textile processing efficiency and product-quality have been commercialized.

The 3/2 twill construction fabric developed for durable-press work trousers is available from Sears Roebuck and Co., and Woolco Department Stores.

Improved all-cotton knitting yarns have been produced from blends of 1-1/16 inch cotton, using standard processing organizations under close laboratory control. One of the country's largest knitwear manufacturers has advised that the yarns are superior to their own produced from higher quality, more expensive cotton, and hence of practical interest to the industry.

The Liquid Cyclone Process pilot plant at Sundatta Oil Mill, Hubli, India (Dorr-Oliver, Inc.), is producing an edible cottonseed flour concentrate and its capacity will be increased from 1 to 5 tons per day. A Liquid Cyclone Process plant for producing 25 tons of high-quality protein flour from glanded cottonseed is under construction at Plains Cooperative Oil Mill, Lubbock, Tex. The plant is scheduled to begin production in 1972. The product, which contains about 70 percent nutritious protein, has the capability of improving human health.

For any successes we have had we are indebted in part to our many friends in State, industrial, and other organizations. A considerable portion of our cooperative research on

cottonseed and linters is supported by funds from the National Cottonseed Products Association (NCPA), the National Cotton Bating Institute (NCBI), and Cotton Incorporated (CI). We are grateful for this encouragement and support.

Probably you are aware that Cotton Incorporated and the International Institute for Cotton, as well as the U.S. Department of Agriculture, conduct cotton research with public funds. We are appreciative because we have the privilege of working in friendly cooperation with these two organizations. It is appropriate to add that we are particularly grateful for the help of CI in commercializing several experimental products, e.g., those that are attractive because of their DP or flame resistant qualities. We are grateful for this help and also because S. Frank Moore and Frank H. Burkitt are on the program to summarize progress in cotton research by their respective organizations.

I wish to thank every one contributing to the success of this conference — the General Chairman, Program Committee, Session Chairmen, speakers, visitors, and the staff of SRRL for the arrangements that have made this conference possible.

I hope your stay in New Orleans will be enjoyable and rewarding. Please visit our Laboratory and talk with our scientists and engineers. We cordially invite you on any occasion during the year to visit us individually or as groups. We shall be glad to have suggestions that will help us make our program more valuable to agriculture and all consumers.

We are honored because Fred R. Senti, who administers the research of USDA's nine Divisions in Marketing and Nutrition Research, is with us. It is my pleasure to present Dr. Senti.

## AGRICULTURAL RESEARCH SERVICE OPERATIONS

by

F. R. Senti

Deputy Administrator

Marketing and Nutrition Research

Agricultural Research Service

U.S. Department of Agriculture

Washington, D.C.

I wish to add my cordial welcome to that already given by Dr. Fisher.

We in USDA's Agricultural Research Service appreciate your interest in cotton research and these annual Conferences.

I wish to take advantage of this opportunity to tell you about some important changes in our Agricultural Research Service.

First, I wish to mention our patents and patent policy. We now have a more flexible patent and licensing policy. As before, non-exclusive licenses may be granted for the practice of our inventions. Under some conditions, however, exclusive licenses may be granted. For the last several years, about 50 patents per year have been granted to inventors of our Southern



Marketing and Nutrition Research Division. Many of them are concerned with cotton and cottonseed development.

Dr. Fisher has already mentioned that cotton research with public funds is now being conducted by various State Experiment Stations, the USDA, Cotton Incorporated, and the International Institute for Cotton. A National Cotton Research Coordinating Committee has been established to facilitate and coordinate this program of cotton research conducted in the United States. Roy Lovvorn, Administrator of Cooperative State Research Service, Washington, D.C., is Chairman of this Committee.

T. W. Edminster, Administrator of USDA's Agricultural Research Service (ARS), recently announced an organizational realignment that reduces the number of lines of supervision at research field locations and, at the same time, provides for strong national research planning.

A research operation staff, located primarily in the field and headed by four deputy administrators, will carry out the agency's research at its present 210 locations throughout the United States. Designated as Acting Regional Deputy Administrators are Steven C. King, Northeast Region; Earl R. Glover, North Central Region; A. W. Cooper, Southern Region; and H. Rex Thomas, Western Region. With this new organization, the Southern Regional Research Laboratory will report to A. W. Cooper, who will be headquartered in New Orleans.

The National Program Staff, headed by four Assistant Administrators, will be located in Washington, D.C., and Beltsville, Md. This staff will function as a mechanism for policy and program development, review, and evaluation on a national basis. It will concentrate upon insur-

ing the proper interaction, balance, and distribution of research effort. The Assistant Administrators will work closely with the Regional Deputies and with other ARS research leaders. Named as Acting Assistant Administrators are Paul D. Delay, Animal Science; Hugo O. Graumann, Plant Science; and Carl W. Carlson, Soil, Water, and Air Research. I have been named Acting Assistant Administrator for Marketing, Nutrition, and Engineering Science.

In announcing the new organization, Mr. Edminster noted that the four Regional Deputies will have major responsibility for the implementation and operation of research programs within their geographic areas. He further pointed out that "They will be close to the work, close to the problems, and close to our key cooperators in the State Agricultural Experiment Stations and in industry." The move will also reduce present multiple lines of supervision to a single supervisory line and will permit reductions in administrative overhead.

The Southern Region will include the States of Oklahoma, Texas, Arkansas, Louisiana, Kentucky, Tennessee, Mississippi, Alabama, Virginia, North Carolina, South Carolina, Georgia, Florida, and the commonwealth of Puerto Rico. Many of these States, of course, are involved in processing cotton.

After the new organization becomes effective on July 1, I anticipate that I shall have more time to devote to program planning and coordination at the National level. I expect to intensify my efforts in research and development concerned with cotton and cottonseed products. I shall welcome your comments on any occasion and the privilege of working with you.

## RESPONSE BY GENERAL CHAIRMAN

by

Robert C. Jackson  
American Textile Manufacturers Institute  
Washington, D.C.

It is a great personal pleasure for me to meet with this distinguished group, and I appreciate the opportunity very much. Over the years, the Cotton Utilization Research Conference has grown into a prestigious and highly successful forum for exchanging scientific and technical information of infinite value to both the raw cotton and the cotton textile industries. The people who have participated in these conferences have made and are making a major contribution toward assuring cotton a significant

place in the rapidly changing textile market.

I must admit to a feeling of inadequacy and perhaps of being misplaced when among the scientific talent that is assembled in this room. At the same time, I am pleased to be a part of this meeting and look forward to working with you over the next 2 days. The people in this room, and some of the ideas and projects on which you are working, will have a tremendous influence on the textile industry for many years to come.

We are meeting at a very crucial period in the long and sometimes difficult history of the cotton industry. There has probably been no previous period when the need for more emphasis on science and technology is more apparent than today. This need extends all the way from the farm to the market place.

Competitive pressures are strong, possibly stronger than at any other time in history. The American consumer has become more selective and more demanding than ever before where quality, style and performance of textile products are concerned.

The needs and the demands of the public are intensified by a growing number of so-called "consumer advocates," inside and outside of government. Many of them view industry as a reluctant and recalcitrant participant in what has become known popularly as the "consumer movement."

This deep involvement with the consumer is nothing new for the textile industry. The terms "consumer" and "customer" have always been one and the same for textile people. Textiles did not become a \$23 billion industry by ignoring the consumer or being indifferent to his or her needs.

The textile industry, like the raw cotton industry, has always placed heavy emphasis on research as a major element in making the American consumer the best clothed and best sheltered in the world.

This emphasis on research and technological development has been hammered into my own thinking and experience during the almost 40 years that I have been involved directly or indirectly with cotton and textiles.

Having grown up in a small cotton farming community in the Mississippi Delta, having had a father who was employed in cotton ginning and oil mill operations, having started my business career as a handyman in a County Agricultural Agent's office in a cotton-growing county, having learned to class and grade cotton as a preliminary to buying it on a commission basis, having been an original employee of the National Cotton Council when it was just an idea, and then having served for 22 years in my present capacity with an industry that during my tenure has consumed more than 200 million bales of cotton, you can well imagine that cotton — its past, its future, its problems, and its opportunity — must constitute an important factor in my life — just as is the case with many of you.

Through all of this period of experience, there has been some understanding of and appreciation for the maintenance of a "place in the sun," so-to-speak, for cotton in the arena of fiber competition.

With all the problems that cotton has experienced, we are sometimes prone to forget the remarkable progress that has been made in cotton growing, harvesting, initial processing, and most certainly in manufacturing and product development. It is a thrilling story that you or I could document in considerable detail.

With this background of experience and accomplishments at all stages of growing and processing, both the raw cotton industry and the textile industry can view the future with a rather sure knowledge that we know where most of the obstacles lie and what must be done to improve. I believe it is clear to all concerned that research — big-time research — on a scale we haven't known in the past, is in the forefront of requirements for success.

If a conference of this nature had been held as recently as 15 years ago, there undoubtedly would have been some discussion about the continuing inroads being made by the man-made fiber and about the likelihood of even better and more diversified man-mades in the future. Some concern might have been expressed over what this was going to do to cotton's favored position in the fiber market. Well, that "future" is now, and consumption of all man-made fibers combined exceeds cotton.

Fifteen years ago, durable press or permanent press very likely would not have received any more than passing mention, if it were discussed at all. Knits, as we know them today, were not in the picture.

Tongue twisting terms like "Phosphorus Trihalide" would not have been part of the textile vocabulary.

Byssinosis was mentioned only in a few medical journals.

But, as we meet here today, these are subjects of prime concern as a result of the veritable revolution which has taken place in the textile industry during the past 15 years.

It is the accomplishments of people like you, combined with changing consumer demands and modern marketing techniques, which have brought about this revolution. It is the combination of these same ingredients which can bring about similarly dramatic changes. Science and research can help overcome some of the basic problems the cotton industry faces today. It is most gratifying to know that cotton now has going for it the most extensive research program ever.

Speaking as a representative of the textile industry, I would like for the next few minutes to explore with you some of these areas which are absolutely critical to cotton's future.

The textile industry is always faced with the need for an adequate and dependable supply of



quality cotton at competitive prices. Since this is a research conference, it would not be appropriate to belabor what is happening to cotton supply and prices at the present time. But, I can guarantee you the impact is severe.

We can only hope that the current uncertainty over the cotton picture will not do any permanent damage to the cotton industry.

Cotton quality, price, and supply are basic factors in determining how much cotton will be consumed. You, as researchers, have an important role to play here, as well as in other areas.

While cotton is faced with many challenges, there are three highly significant areas, any one of which will have a major impact on your industry, and which in combination can make or break cotton. In each instance, successful research is the key.

First is the matter of fabric flammability.

Like so many of the problems we have as a Nation and as an industry, there is no simple or pat solution to the problem of fabric flammability. Everyone admits that fabric burns and that people are at times seriously injured or killed in fabric-related fires.

You have on your program a number of speakers who know a good deal more than I about fabric flammability and what the industry is doing to overcome it. You will be hearing from them tomorrow, so I will not attempt to go into the subject in any detail.

What I would like to emphasize, however, is that a solution to this problem must be found, particularly where cotton is concerned, and it must be found as quickly as possible. It must be found, first, because it is the right thing. We all want to do everything humanly possible to reduce fabric-related injuries and deaths.

There is a tremendous financial incentive for the individuals and the companies who make the breakthrough, something which some of our critics tend to overlook. Like that better mousetrap, the world will beat a path to the door of the man who succeeds.

A second critical area is durable and permanent press.

Cotton still has a long way to go where permanent press is concerned. It is always difficult to alter nature, which is why progress has lagged in this area. The physical properties that have made cotton so utilitarian and popular, apparently work counter to the physical properties needed for good durable press.

So, it is the textile and cotton scientists who hold the key to a really successful durable-press breakthrough. Here, once again, the rewards will be tremendous.

And, finally, we have the matter of Byssinosis. I cannot overstate the seriousness with which

our industry views this problem that is now so clearly identified with cotton. It has the potential for driving mills away from cotton, irrespective of improvements on other fronts, unless a solution is found in the reasonably near future.

Both the National Cotton Council (NCC) and Cotton Incorporated (CI) have recognized Byssinosis as a problem. The Council, at its annual meeting this year, adopted a strong resolution calling for stepped-up research into all aspects of the problem, and authorizing a joint committee of NCC, CI, and ATMI representatives. The first meeting of that committee was held in our Washington office just last Thursday, and we are encouraged by the prospects of closer coordination and increased emphasis.

Cotton Incorporated has important research underway, and more under consideration. We have spent well over a quarter of a million dollars on the subject and our member companies a great deal more.

This is a good start, but these efforts must be supplemented and intensified throughout the cotton industry. I strongly recommend that the U.S. Department of Agriculture recognize Byssinosis for what it is — first, a cotton-related disease that impairs health of human beings; and next, a problem that will drastically curtail consumption of cotton, unless eliminated, and that very soon.

Our concern over these problems, serious as they are, can be alleviated. If we reflect on all that this industry has been able to accomplish in the past, once it recognized a problem and went to work on it.

Many of these accomplishments have come from the laboratories of our textile companies and their suppliers. Others have come from government research.

When the American housewife told us she was tired of the drudgery of ironing, the textile industry and its scientists gave her no-iron and fitted sheets.

When the lady said she wanted brightness and fashion in her home as well as her wardrobe, we gave her printed sheets and bedspreads and color-coordinated towels and wash cloths.

We even spruced up the man around the house with colored and printed shirts, and splashy color in sports and even business attire.

At the same time, our manufacturers have made textile products more durable and kept prices down.

But no one can rest on his laurels — not if he expects to remain a factor in today's highly competitive marketplace.

At the conclusion of these 3 days of evaluation of current scientific projects, I hope we all will leave with a new spirit of dedication

to finding the right answers to those questions which will determine the very future of the cotton industry in America. I believe we all

agree that the know-how is right here at this conference, so let's get on with the job.

## COTTON INCORPORATED ACTIVITIES

by

S. Frank Moore  
Cotton Incorporated  
Raleigh, N. C.

It is my pleasure to meet with you today. I will try to inform you of the "Activities of COTTON INCORPORATED" during the past months.

Our Company is owned by the 300,000 cotton growers in the United States. We are dedicated to help them make a profit growing cotton. We try to accomplish this through Research and Technical Service located at Raleigh, N. C., and with our Sales and Marketing Divisions in New York, Dallas, and Los Angeles.

We not only do research on products, but also Agricultural, Processing, Handling, and Services Research, from the soil study through wear testing of garments.

Boll Weevil Eradication effort shows fine possibilities for great success. We have not completed the first year of the experiment, however, we can see "spin offs" that will be extremely beneficial whether or not we are successful with the original goal of total eradication:

(1) Research supported by this project shows that up to 90 percent of weevil populations can be lured to 10 percent of the cotton acreage with the use of phenomone traps.

(2) Earlier than normal strip plantings of Temik-treated cotton combined with the sex lure, can be an economical means of lowering weevil populations.

(3) The development of the Leggett Trap shows promise for lowering the cost and increasing control of the weevil.

We hope this is the beginning of the end for America's "No. 1" cotton pest.

We have recently released results of years of research that can save the grower \$24 a bale by more efficient use of manpower and equipment from the stalk to the bale. We have made a 20-minute movie on this and there are 30 copies in constant use. This film is generating tremendous interest all across the cotton belt.

At COTTON INCORPORATED, we have a total Marketing operation. Three merchandising managers backed up by Technical Service, Product and Process Development and Research.

Our *Technical Services Department* is in full swing. This service is available to anyone processing cotton and is being used weekly by the mills.

### DURABLE PRESS RESEARCH

We are currently trying to exploit two DP processes of merit which have emerged from previous CI sponsored research. The first is the vapor phase process, which I am sure most of you know is now commercial. Its particular merit is the high level of DP performance attained which is particularly noticeable when severe laundering methods are used. This is why it is a natural for rental uniforms, and there will probably be a spillover to career apparel. We also see terrific advantages for dress shirts even when laundered under domestic laundering conditions. The appeal to the public that we can rely on is not only the superior DP performance, but also retention of better absorbency and soil release which, of course, would be accentuated by introducing products which contain more than the normal amount of cotton. For example, in shirts we believe a 60/40 cotton/polyester blend may be optimum.

The second process is pad/vapor/set whose advantages are specific to cotton, because of a better retention of strength and abrasion resistance. We are cooperating with a mill organization in the further development of this process. Both the process itself and the way we are trying to exploit it resemble the Southern Regional "Polysat" development.

Although our proprietary interest in these two processes gives us some advantage, it is worth stressing that we are on the look-out for processes, whatever their source, which could be exploited to cotton's advantage.

The rest of our DP research program can be divided into three categories.

The first involves developing processes which are less dependent on crosslinking to attain DP performance.

The second involves combining swelling and stretching operations to reduce the irregularities of the cotton fiber and make it a better



substrate to work with.

The third is to develop improved blending technology so that the synthetic "reinforcement" takes a greater share of the load, especially in high cotton blends.

These studies are mainly still at the lab and pilot-plant stage, but some are showing promise of lifting strength retention, for example, to the 70 to 80 percent retention level for all cotton.

#### FLAMMABILITY RESEARCH

Research at the Southern Marketing and Nutrition Research Division (SMNRD) has produced a valuable basis for developmental work by many cotton textile organizations. However, in all too many cases, their work has not been carried to full commercial development, for reasons of money, lack of proprietary interest, or others. This being so, the cooperative arrangement between the SMNRD and COTTON INCORPORATED on the development of the THPOH/ammonia finish is particularly meaningful, and represents about as fine an example as I have seen of a good working relationship between an industrial organization and this fine government laboratory.

We have entered into a contractual agreement with a large finisher of textile goods to commercialize the THPOH/ammonia finish, with representatives of SMNRD cooperating in an advisory capacity. Our contractor and ourselves are sharing the costs, and we have established a full-scale processing line to work out in a full-scale process the time, temperature, and concentration variables so that this very promising flame retardance treatment can be used in commerce.

Why was THPOH/ammonia selected from the many candidates we could have chosen? Well, the reasons are primarily these:

It is the only fire retardance finish we know of which results in no loss of strength, and which with the proper amount of softener will give 100 percent strength retention with only a modest loss in tear strength. Second, it was a process which seemed to us to offer an excellent chance of lending itself to commercial application, because we thought we knew why those firms (and there were many of them) that had tried the process, had failed to make it work adequately.

The preliminary trials have shown real promise, although we have not succeeded to the point where we can with confidence manufacture goods guaranteed to meet the Federal Flammability Standard on Children's Sleepwear. However, we have every confidence that this is only a matter of further development, and we

believe this process will be on stream by the end of this year. When the problem is solved, the technology will be made available to all finishers who want to use it, on an equal basis.

We allocate a very major proportion of our total flammability research budget to the development of improved flame retardants, and in this work we are following the course that most of you logically would follow. We are attempting to make fire retardants that are effective at lower add-ons, less costly, and less harmful to desired fabric qualities. For example, we are synthesizing compounds which are rich in phosphorus and nitrogen; and we have obtained in laboratory quantities, two candidate materials, that are effective at low add-ons. We cannot say at this point when or even if these candidates will reach the market; but we can guarantee that if it can be done, the people working on the problem are competent to do it.

Early this year we broke ground for a new Research Center in Raleigh, N. C. Before the Company's move to Raleigh from Memphis, we did not have any In-House Research facilities. On the start-up in Raleigh, we put in a Research and Fabric Evaluation Laboratory. In our new Research Center this laboratory space will be increased. We are also putting in a Biochemical Laboratory and a Product Development Laboratory. This Product Development Laboratory represents an investment of over \$400,000 in knitting machines. We see a very real opportunity for Cotton in Knitting. Already, we see double knits taking in blends. We are working on surface treatments for cotton and high cotton blend yarns for knitting.

Research is being done in breeding, growing, harvesting and ginning to improve the fiber for knitting.

A few words concerning COTTON INCORPORATED's Byssinosis research program are probably in order at this time. As you may know, passage of the Williams-Steiger Occupational Safety and Health Act of 1970, set the stage for the U.S. Labor Department to apply Federal standards established under the Walsh-Healey Act to the textile industry. On January 25, 1972, the Labor Department announced that five target health hazards had been identified. These included carbon monoxide, silica, asbestos, lead, and cotton dust. We were extremely surprised to find ourselves, cotton dust, affiliated with such toxic materials. Certainly, while cotton dust may incite respiratory problems in textile mill workers it is by no means in any sense nearly as toxic as the above-mentioned materials. An old dust standard of 1 mg. per cubic meter was invoked by the Labor Department and this left the cotton industry with a

new acute problem. This action had been anticipated by many organizations including COTTON INCORPORATED and a backlog of good sound information is available for dealing with it. Nevertheless, more information is badly needed and COTTON INCORPORATED has developed an intensive research program at the medical-chemical, breeding-cultural, and ginning-processing level to deal with the Byssinosis problem. The objectives of this program are to: (1) develop adequate methods for detecting and measuring Byssinosis; (2) identify both botanically (plant part or parts) and chemically (specific compounds) the causative agent or agents; (3) eliminate through plant breeding the causative agent or agents and reduce total trash generating capacity of cotton by utilizing plant characters such as smooth leaves, okra-shaped leaves and frego bracts; (4) reduce total trash in cotton through improved cultural practices such as short season cotton, improved harvest-aid chemicals, and better ginning and cleaning; and (5) develop ginning and processing methods to inactivate the causative materials in cotton.

The last objective is being vigorously pursued jointly with Burlington Industries. A new process has been developed by Burlington to eliminate Byssinosis at the plant level. COTTON INCORPORATED is working with them to accelerate the use of this promising technology. This is a temporary relief measure. COTTON INCORPORATED's Byssinosis research program is designed to completely eliminate the problem.

One of the best things that has ever happened for Cotton Research was the formation of the 13-man National Cotton Research Coordinating Committee last year. These committee-

men are from the USDA, State Experimental Stations of the land grant universities, and COTTON INCORPORATED. We can now review each others research efforts and make every dollar involved in cotton research go much further and avoid duplication of research.

One of the hardest things in research is to know when to stop a project. We will not do research for the sake of doing research. When we feel we are going up a blind alley, we will terminate our effort, take our loss of investment, and move to more promising areas. In research, you certainly cannot always be right.

At COTTON INCORPORATED, we have 46 *Directors* and all produce cotton. They are always involved in the decisionmaking — not only in research, but complete Company activities.

Before closing, I want to cover our Company's other half located in New York — The Sales and Marketing Division. This group is doing an excellent job with the mills' merchandising and sales people in New York. There are many ways to promote cotton and they are leaving no stones unturned. With new *innovations in fabric and styling* they are showing the Fashion People, from a creative approach, how to use more Cotton.

You are here for 3 days and a lot of chemistry. So, I thought, for a change, you would like to see one way that COTTON INCORPORATED promotes its fiber. The great spirit of the Dallas Fashion Show has been captured in all its color on this short film. *THE COTTON FEEL OF '72*.

Again, it has been my pleasure to be with you here in New Orleans.

## COTTON RESEARCH AT IIC

by

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*The Easy-care Problem.* — The Technical Research Division of International Institute for Cotton (IIC) was created 5 years ago. This is, therefore, an opportune time to review progress, to discuss the many current problems, and to identify those areas where IIC can operate most effectively in the future.

During this period, the objective which has been given the highest priority is a solution to the problems of easy-care. It is relatively simple to give cotton excellent easy-care properties, but in the process the strength and durability of the

products are frequently reduced to an unacceptably low level. It is the maintenance of the strength and durability characteristics which is the real problem of easy-care.

During the last 50 years, virtually all the attempts which have been made to find a solution to this problem have been through the empirical use of a wide variety of chemicals or by minor modifications to the method of their application to the cotton fabric. The IIC view was that this well trodden path was unlikely to lead to any significant new developments and



that much more attention had to be paid to the substrate which was being treated. Answers were needed to such questions as:

Why are cotton products in general weaker than the synthetics?

Why does cotton lose strength and durability when subjected to easy-care finishing?

What modifications can be made to the fiber, yarn, or fabric in order to maintain durability after easy-care finishing?

As a result of the research program, we have instituted and from work carried out by the Southern Regional Research Laboratory (SRRL) scientists and others, we now have some of the answers to these questions and a much better understanding of the structure of the cotton fiber. We have demonstrated that:

- a. Cotton fibers can be strengthened considerably by reorganization of the fibrillar structure.
- b. The magnitude of the strength improvement depends very markedly on the variety and/or growth conditions of the fiber.
- c. When these toughened fibers are treated with high levels of easy-care chemicals, there is little or no loss in strength or toughness.

From these results we have concluded that in order to produce easy-care cotton fabrics with excellent durability, it is highly desirable to achieve three objectives:

1. Uniformity of fibrillar structure within most fibers in a fabric.
2. Elimination of all residual stresses in the fabric caused by sizing, weaving, etc.
3. Uniform distribution of the easy-care chemicals throughout the fibers and yarns in the fabric.

We have applied these principles to fabric processing on a laboratory scale and have demonstrated that it is possible to achieve excellent easy-care performance, coupled with an abrasion resistance close to that of the untreated cotton fabric.

From all these findings it is possible to define both a short term and a long term solution to the problem of easy-care. The short term solution is for the finisher to modify his method of mercerization and resin application in order to obtain the best results from the cottons which are available today. Improved techniques of mercerization will achieve the first two objectives listed above and new methods of application of easy-care chemicals will achieve the desired uniformity of distribution. IIC is working intensively in both these areas in order

to translate the laboratory results mentioned above into commercial methods applicable on full scale machinery.

By this approach, we are convinced that the finisher can produce easy-care fabrics definitely superior to any available commercially today, but he is, of course, limited by the properties of the raw cotton on which he has to operate. The long term solution is for the grower to develop improved varieties of cotton which will respond more favorably to the processes of easy-care finishing. Before this can be done however, the finisher has to define — in terms of fiber structure — what are the desirable fiber characteristics and test methods must be developed to enable the cotton growers and breeders to identify and measure these characteristics in their selection programs. This is clearly a long-term program, but we have research projects aimed at providing this information.

*Product Development.* — While this basic work was being carried out, IIC initiated a product development program which is concentrated in two main areas:

*Knitting* — IIC now has its own small knitwear development unit and is studying the utilization of new and conventional cotton yarns on new and conventional knitting machinery. Individual projects include the development of double jersey knitted cottons, the application of break spun and ammonia treated yarns in knitwear and the use of compound needle machines for the warp knitting of singles yarns. In order to exploit fully these new or improved fabric properties, it is necessary to pay the most careful attention to design, coloring, and styling if they are to attract the interest of the maker up. Close working relationships have therefore been established with the fashion advisors and marketing experts of our promotion division in order to ensure the most effective presentation. This relationship works well in both directions for we are often able to advise our fashion and marketing experts on ways of improving the practicability of some of their more bizarre ideas for fabrics and garments.

*Finishing.* — The development work in this area is aimed at two important markets for cotton — sheetings and workwear. With the heavier weight fabrics, which in Europe are still acceptable for these two purposes, it is

possible to obtain a good easy-care performance coupled with an adequate durability and a number of manufacturers in Europe are marketing 100 percent cotton easy-care sheets. There is, however, a trend towards lighter weight products and while we are hopeful that our improved easy-care finishing procedures will enable us to obtain satisfactory results on all cotton product, it is possible that small amounts of nylon or polyester may be needed as reinforcement if conventional finishes are to be used. We are, therefore, studying the existing cotton-rich blends which are on the market and also instituting our own development program on these materials.

*Cooperation with Industry.* — IIC recognizes very clearly that it can only achieve its objectives through close cooperation with all levels of the textile trade. In the technical work, for example, it is necessary to work closely with the leading textile mills and our influence is proportional to the commercial potential and feasibility of our ideas. We believe that we can offer profitable advice to the mills in four main areas:

1. The results of our basic research program. These have already led to the development of improved processes for cotton by a number of European mills.
2. New products from our development program. Again, we know of several mills who are using products and processes developed by our efforts.
3. Know how and technical information. We have recently started technical service operations in Europe and Japan in order to channel relevant information into the industry, to organize and implement cooperative trials and to provide technical assistance with problems of cotton processing.
4. Assistance with the development of products and processes by industry groups. For obvious reasons, much of this work has to be done on a confiden-

tial basis, but we have been able to make significant contributions in this field.

*New Processing Requirements.* — Due to the pressure on margins, mills are increasingly looking for more productive machinery and for simpler processing procedures, and the textile machinery industry is working hard to provide the needed equipment. Most of the new developments in this field come from Europe and Japan and we recognize the importance of ensuring that both the problems and opportunities for cotton on the new machines are recognized and acted upon. We are concentrating on those developments which are of a special importance to cotton — such as liquid ammonia processing, compound needle knitting machines, and twistless spinning, but many others are being watched closely. One general area is the replacement of weaving by knitting: already for example, corduroy fabrics can be knitted at ten times the normal weaving speeds, but the fiber content is 80 percent cotton/20 percent nylon. Naturally, the corduroy manufacturers are very interested in this development, but they prefer a 100 percent cotton product; we are working very hard to provide them with such a product.

*Need for Vertical Approach.* — We are working in an industry subject to very rapid changes. Once upon a time, a cotton farmer had only to satisfy the needs of a ring spinner, whose output was utilized largely by weavers for the production of untreated fabrics. Now, new methods of spinning are taking a firm hold, especially in Japan, and these make new demands on the fiber quality. Knitwear is gradually taking a larger share of the apparel market, and an increasing percentage of cotton fabrics are given some form of easy-care finish. These changes are bound to have an influence on the demand and quality requirements for cotton in the future. The cotton farmer himself is in no position to be able to judge the nature and extent of this impact. We in IIC are in close touch with all these changes that are taking place in Europe and Japan. We believe that one of our roles is to provide the necessary feedback of information to the farmer in order to help him select and produce the type of cotton which will be best suited to the modern industry and consumer.



## PROTON MOBILITIES OF LIQUIDS SORBED ON COTTON CELLULOSE

by

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(Presented by Donald P. Miller)

The mode of sorption of various liquids on cotton cellulose has been investigated by means of proton magnetic resonance spectroscopy (NMR). In particular, pulsed NMR spectroscopy is extremely useful for examining the relaxation processes of the spins associated with protons of sorbed liquids. In general, the parameters measured by pulsed NMR, the spin-spin and spin-lattice relaxation times, reflect the interactions of the nuclei with each other and the surrounding lattice. These interactions are dependent on the relative motions or vibrational spectra of these bodies as compared with the resonance frequencies employed in the measurements. In general, the smaller the relaxation times of the nuclei in sorbed liquids the more tightly bound, and hence the more restricted the motion. In addition, it is not uncommon for protons in sorbed liquids to exhibit multiple spin-spin and spin-lattice relaxation times thus indicating more than one mode of sorption.

To compare the results of these NMR observations with other data related to sorption processes, the data obtained from previous work at the Southern Regional Research Laboratory on swelling of yarns in various liquids was used as a reference. These data<sup>2</sup> consist of microscopical measurements of the swelling of fibers in the solvents which were in turn compared with the number of turns that a cotton singles yarn untwists when placed in the solvent. It can be shown by theoretical and statistical methods<sup>3</sup> that the relationship between the untwisting of the yarn and the swelling of the fibers can be approximated by the equation

$$a = (\Theta_1 / \Theta_2)^{1/2}$$

where  $a$  is the ratio of the swollen diameter of the fiber to the original diameter and  $\Theta_1$  and  $\Theta_2$  are the number of twists in the yarn before and after swelling, respectively. The data in this

investigation, which included a broad range of organic solvents and inorganic solutions, were reported in terms of "swelling index" given by the relationship  $I = (\Theta_1 - \Theta_2) \cdot \text{solvent} / (\Theta_1 - \Theta_2) \text{ water}$ . Thus the ratio of the number of turns the yarn untwisted in the solvent to the number of times it untwisted in water is used as a measure of the swelling power of the solvents.

The relaxation times of the samples were determined by standard pulsed NMR techniques<sup>4</sup>. The spin-spin relaxation times were determined by the Hahn spin-echo method. In this technique, a pulse of duration  $t$ , such that  $\gamma H_1 t = \pi/2$  where  $\gamma$  is the gyromagnetic ratio and  $H_1$  the RF field strength in the probe of the spectrometer, is applied to the sample. After a suitable length of time  $t$ , a second pulse of duration of  $2t$  is applied to the sample. At the time  $2t$ , an echo signal is observed by the instrument. Semilog plots of the intensity of the echo signal against various values of  $t$ , are then made and the spin-spin relaxation time  $T_2$  determined from the slope. A similar technique is used in the determination of the spin-lattice relaxation time  $T_1$ . The method is referred to as the  $90^\circ$ - $90^\circ$  pulse method since two pulses of duration  $t$  as given in the equation above are used. The intensity of the signal immediately after the first and second signals are measured and their difference determined. Semilog plots of the difference versus the time interval between pulses  $t$ , for various values of  $t$ , are made the  $T_1$  determined from the slope.

The samples were prepared by placing 80x80 printcloth and adding the solvent in aliquots of several drops. The tubes were placed in the instrument probe and the signal observed after each addition. When a signal strong enough to produce a signal to noise ratio of about 10 to 1 was observed, the measurements of the relaxation times were made. Thus the concentration of solvent on the samples may be regarded as the

<sup>1</sup>Visiting Scientist from Clemson University.

<sup>2</sup>Porter, B. R., and Orr, R. S. Textile Res. Jour. 35: 159-167. 1965.

<sup>3</sup>Pittman, R. A. Textile Res. Jour. 36: 1020-1021. 1966.

<sup>4</sup>Farrar, T. C. Pulsed and Fourier Transform NMR. Academic Press. New York, N. Y. 1971.

minimum to produce an adequate signal.

The following solvents were observed: benzene, 2-propanol, methyl alcohol, ethyl alcohol, morpholine, water, dimethylsulfoxide, and ethylenediamine. The solvents are listed in order of increasing swelling index. The first five, benzene through morpholine, had swelling indices from 0 to 0.33 and  $T_1$  values (milliseconds) from 1300 to 150. The next group, water and dimethylsulfoxide, had swelling indices of 1 and 1.2 and  $T_1$  values of 200 and 180. The ethylenediamine has a swelling index of 2.9 and  $T_1$  of 110. Thus, generally, the greater the swelling power of the liquid the smaller the spin-lattice relaxation time. The spin-spin relaxation times were about one-tenth the spin-lattice times and bore a similar relationship to the swelling indices. Both the spin-spin and the spin-lattice relaxation times of the pure liquids were much larger than that observed for the sorbed liquids. These data indicate that the greater the swelling power of the liquid the more tightly bound and immobilized it is on the cellulose.

In addition to the organic solvents studied, a series of aqueous solutions of NaOH ranging

from 0 to 25 percent concentration were investigated. Cotton linters were saturated with the solutions then pressed to remove excess liquid. As the concentration increased from 0 to 12 percent,  $T_1$  decreased from about 500 milliseconds to about 180 milliseconds. As the concentration increased beyond 12 percent, it became evident that the protons were in two distinct states of sorption as evidenced by the existence of two spin-lattice relaxation times. The more tightly bound portion of the protons (calculated to average about 25 percent with considerable scatter) exhibited a  $T_1$  of about 50 milliseconds with a tendency to decrease over the range 12 to 25 percent concentration. The remainder of the protons observed had  $T_1$  equal to about 190 milliseconds. The appearance of multiple spin-lattice relaxation times at 12 percent concentration is significant inasmuch as this is the minimum concentration at which mercerization will take place at room temperatures. The observations made in this work were restricted to these protons associated with the liquids sorbed on the cotton since instrumental parameters prevented the observation of the cellulose protons.

## THE POLYMORPHS OF CELLULOSE

by

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(Presented by Alfred D. French)

D. W. Jones (5), after an exhaustive study of cellulose structure, concluded in 1960 that no conventional arrangement of twofold screw axis chains can provide the X-ray intensity distribution found for native cellulose. With the aid of modern computers and recent information about residue conformation (4, 1), we have been re-examining the cellulose structures. Since only a small amount of information is available from any one cellulose X-ray diagram, we have decided to study several of the polymorphs and to try to correlate the results.

Five distinct polymorphs which are apparently composed of only cellulose have been recognized. In recent years, investigators have also added subscripts to cellulose III and IV to indicate whether their origin was cellulose I or cellulose II. Of the total of seven, I, II, III<sub>I</sub>, IV<sub>I</sub>, and III<sub>II</sub> are currently under study here; cellulose IV<sub>II</sub> and cellulose I are not under consideration at present.

One question debated throughout the his-

tory of cellulose structural investigation has been the presence of odd-order meridional reflections (10, 8). We chose the precession technique to investigate these reflections because the need to tilt the fiber is eliminated. In addition, we have learned that the Lorentz corrections for meridional intensity measurement are possible for the precession instrument (7) but are exceedingly difficult for the tilted fiber techniques using flat-plate or cylindrical cameras (3).

We have been able to learn a substantial amount of information from these photographs. Cellulose I, III<sub>I</sub>, and IV<sub>I</sub> do not have twofold screw axis chains; distinct odd-order meridional reflections are definitely present. The intensity of these reflections is rather low, but their complete *absence* is required if a twofold screw axis is present. Moreover, intensity calculations show that only low values are expected, even with substantial deviations from twofold screw axis conformations. Cellulose II (Fortisan) dia-



grams, on the other hand, show no odd-order meridionals, but one can only say space group  $P2_1$  is a possibility for cellulose II. Cellulose III<sub>I</sub>, while being much less crystalline than cellulose II, appears to have the same meridional intensity distribution as cellulose II, so here again, space group  $P2_1$  is a possibility. Otherwise, the possible space groups are P2 and P1 for all the polymorphs. Space group P2 can only have parallel chains with no relative translation, while P1 can have either parallel or anti-parallel chains with any amount of translation. If the space group is P1, as has been established for native *Valonia*, then the angles  $\alpha$  and  $\gamma$  of the triclinic unit cell must be very close to  $90^\circ$ .

Different values for the meridional intensity ratios are found for cellulose I, II, III<sub>I</sub>, and IV<sub>I</sub>. T. Kubo (6) correctly understood the reason for the differences in meridional intensities in 1940 after using an oscillating fiber technique. Essentially, the chains must either be translated relative to each other or the position of some reasonably heavy group, such as oxygen (6) must change dramatically to account for the differences among the polymorphs.

The equatorial intensities point up the other major differences among the polymorphs, i. e., the size, shape, and packing of the unit cell. Measurements of the precession photographs, using all the reflections, have given support to Wellard's values for cellulose I (9); necessitated a small change for cellulose II; confirmed Barry, Peterson, and King's values for cellulose III (2), (thereby refuting Wellard's values); and required a small change for cellulose IV. Using these unit cell values, and equatorial intensity values, Fourier maps have been prepared which illus-

trate the general position of the chains within the unit cell. Since the packing of the cellulose III<sub>I</sub> and cellulose III<sub>II</sub> unit cells is essentially the same, while the meridional intensities are very different, it is concluded that there is most likely an important difference in the position of oxygen (6). The Fourier maps may also be used to fix the location of complexing molecules in cellulose complexes. A map of the N-methyl-1, 3-propanediamine cellulose complex shows that the complexing molecules are arranged in double rows between the rows of cellulose chains.

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## INTERACTIONS OF ANHYDROUS AMMONIA AND ORGANIC SOLVENTS WITH COTTON AS MEASURED BY THE ESR TRAPPED RADICAL TECHNIQUE

by

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(Presented by Jett C. Arthur, Jr.)

The textile properties of cotton are dependent on its natural fibrous and molecular structures. During the modification of the properties of cotton the interactions of different solvents and solutions which alter these natural structures are particularly important. The effects of these interactions may be divided into three general classes, as follows: (1) the crystal lattice structure of cotton is either reversibly or irreversibly altered; (2) the accessibility of the

hydroxyl groups on the cellulose molecule to chemical reagent is changed; and (3) the morphology of the fibrous structure is changed. In practical applications most of the solutions used have been aqueous. More recently there has been considerable interest in the possible practical use of organic solvents and ammonia in textile finishing. Generally, the interactions of solvents and solutions with cotton have been evaluated by determining the properties of

cotton textile products prepared under different experimental conditions.

In this discussion, applications of SMN's electron spin resonance trapped radical technique to the evaluation of the interactions of solvents and solutions with cotton are outlined. Cotton is irradiated by high energy ionizing radiation, such as cobalt-60 *gamma*-radiation, to a dosage of one megarad or less. At this dosage, dehydrogenation reactions of the cellulose molecule are initiated. Trapped free radicals are formed within the cellulosic structure. Then the interactions of various solvents and solutions with cotton under different experimental conditions are evaluated by the rate and selectivity of the scavenging of the trapped cellulosic free radicals. It should be emphasized that at the radiation dosages used only very small changes in the textile and chemical properties of cotton are recorded. Also, the electron spin resonance technique makes possible a more dynamic evaluation of the interactions of solvents and solutions with cotton than the usual product property methods.

Most of the interactions of solvents and solutions were determined with irradiated cotton cellulose which initially had crystal lattice types I and II. Cotton cellulose II was prepared from cotton by the usual mercerization techniques. Interactions of both liquid and gaseous water with cotton, which had been ball-milled and decrystallized with ethylamine and had lattice types III and IV, were also determined. Aqueous solutions, which contained inorganic solutes, used included solutions of sodium hydroxide and zinc chloride. Organic solvents, to which different amounts of water were added, used included acetone, acetonitrile, ethanol, N, N-dimethylformamide, dimethylsulfoxide, and methanol. The interactions of both liquid and gaseous anhydrous ammonia with cotton were recorded. The effects of interactions of solutions with the trapped free radicals in cotton to initiate chain reactions with one or more of the components of the solution were also determined by both electron spin resonance spectroscopy and product formation.

The scavenging of trapped radicals by water (both liquid and vapor) were dependent on the lattice type and temperature. For example, about 70 percent of the radicals formed in irradiated cotton cellulose I and about 90 percent of the radicals formed in irradiated cellulose II are scavenged by contacting the samples with water, particularly at above room temperatures. In ball-milled and ethylamine-

decrystallized cotton almost all of the free radicals were scavenged by water. Differences in hydrogen bonding in the irradiated cottons, which had different lattice types and were contacted with water, were reflected in the hyperfine splittings of ESR spectra recorded.

Interactions of cotton with solutions of sodium hydroxide and zinc chloride were dependent on concentration of the solute. In the case of cotton cellulose I interaction of solutions of sodium hydroxide reached a maximum when conversion of lattice type I to II occurred. Maximum interaction of solutions of zinc chloride with cotton occurred at about 70 percent salt concentration. The apparent rates of diffusion of selected organic solvents into cotton were as follows:  $\text{H}_2\text{C} > \text{CH}_3\text{OH}, \text{CH}_3\text{COCH}_3 > \text{DMSO} > \text{DMF} > \text{CH}_3\text{CN}$ . The apparent rates of diffusion of pure solvents into cotton were the reverse of those of aqueous solutions of these solvents into cotton. This may reflect differences in molecular association (solvation) for each of these solvents with water.

Anhydrous ammonia (gas) at 25° C. and atmospheric pressure acted as a weak swelling agent for cotton cellulose I and increased the vibrational state of the cellulose chains, particularly in the highly accessible regions, so that recombination of some of the free radicals occurred. When cotton cellulose I was contacted with anhydrous ammonia (liquid), most of the free radicals were scavenged. After the ammonia (liquid) was removed, apparently changes in the lattice type and degree of order in cotton increased the accessibility of the remaining free radicals, so that they were readily scavenged by water.

Interactions of solutions of vinyl monomer with the trapped free radicals in cotton to initiate chain copolymerization reactions were dependent on lattice type and composition of the solution. For example, from water the extent of copolymerization of ethyl acrylate with irradiated cotton cellulose I was greater than with cotton cellulose II; from methanol the extent of copolymerization with irradiated cellulose II was greater than with cellulose I. From methanol (40 vol-percent) — water (60 vol-percent) maximum extent of copolymerization occurred with both irradiated celluloses; however, the extent of copolymerization was less with irradiated cellulose II than with cellulose I.

Possible applications of these types of data in the development of solvent finishing processes for cotton were discussed.



## ELECTRICAL PROPERTIES OF COTTON

by

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(Presented by J. M. Hemstreet)

To provide specific information necessary for the development of a new textile processing system based on conveying and manipulating cotton fibers by electric fields, some of the theoretical aspects of a fiber's electrodynamic behavior in uniform and nonuniform fields have to be considered.

The forces on charged fibers in a field are predominately coulombic when the fibers are far from the boundary surfaces. If the fibers approach to within a centimeter or less of these surfaces, other forces, such as mirror and dielectric forces, began to effect the behavior of the fibers. To better understand and predict the movement of fibers in electric fields having either conductive or non-conductive boundaries, it is necessary to measure the dielectric constant and the charge on the fibers.

The measurement of the charge is made by one of two methods depending on the size of the sample. For fiber aggregates of approximately 20 mg. a torsional method is simple and gives consistent results. The apparatus consists of two adjacent sets of parallel plate electrodes within an insulated box. A nylon rod sample holder is suspended by a perpendicular steel fiber of known torque constant with the end of the rod in the center of the electrode configuration. The steel suspension is connected to a calibrated indicator for measuring the angular displacement of the nylon rod.

In operation, the electrodes were raised to some given potential, then a sample attached to the end of the nylon rod was touched to the charged electrode and released. A torque was developed in the suspension, the value of which could be determined by measuring the angular deflection of the suspension. The angular deflection or torque is equated to the force on the cotton fiber sample due to the charge on the fiber. Figure 1 gives the relationship of charge on a sample as the electric field intensity is increased. Charge values reach as high as  $10^{-8}$  coulombs. These results show a quadratic relationship

$$F = kV^2$$

where  $F$  is the force,  $V$  the voltage, and  $k$  is a proportionality constant. The relationship is

quadratic because the charge on the sample is a direct function of electrode voltage and the force is a linear function of the charge.

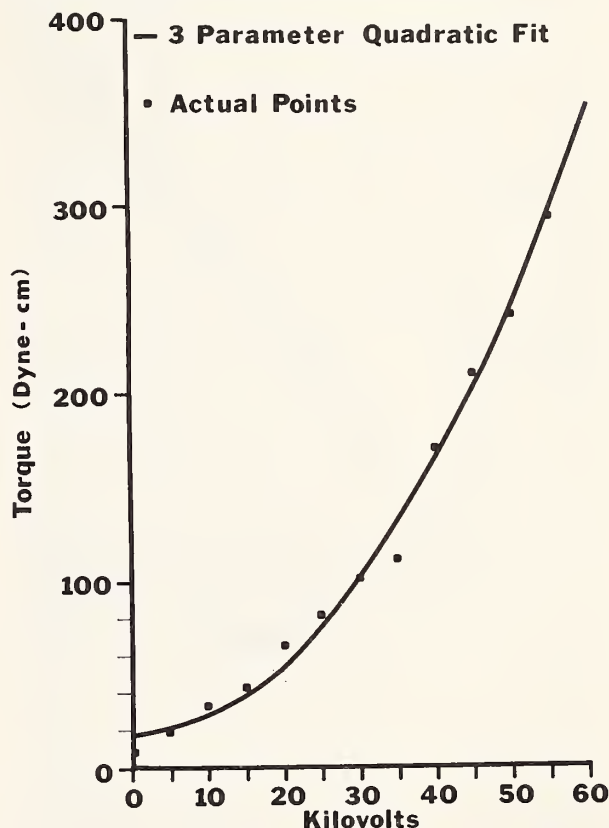


Figure 1. — Torque on fiber aggregates of increasing charge.

Figure 2 is the plot of the force on a sample of cotton that has been initially charged to a specific potential of 40 KV and then placed in a field of increasing intensity. This relationship is linear and of the order of magnitude of  $10^{-9}$  coulombs.

Measurements of charge on individual fibers can better be accomplished by the direct balance method. A fiber is suspended from an electrobalance directly into an electric field so that when the field is energized the force of the field on the charged fiber is directly measured. Figure 3 gives the relationship of the force on a single

fiber, previously charged to 40 KV, as a function of a varying field. This relationship is linear to a value of 14 KV; at higher potentials the charge tends to leak off the fiber. The charge on single fibers reached a value of approximately  $10^{-10}$  coulombs, giving a much higher charge to mass ratio than for a cluster of fibers.

$$F = a E \frac{dE}{dx}$$

where  $E$  is the electric field and the product  $a E$  determines the polarization of the material.  $dE/dx$  is the differential force acting on the polarized sample in the direction of the increasing field. It must be noted that if the field is uniform,  $F$  disappears since  $dE/dx$  is zero.

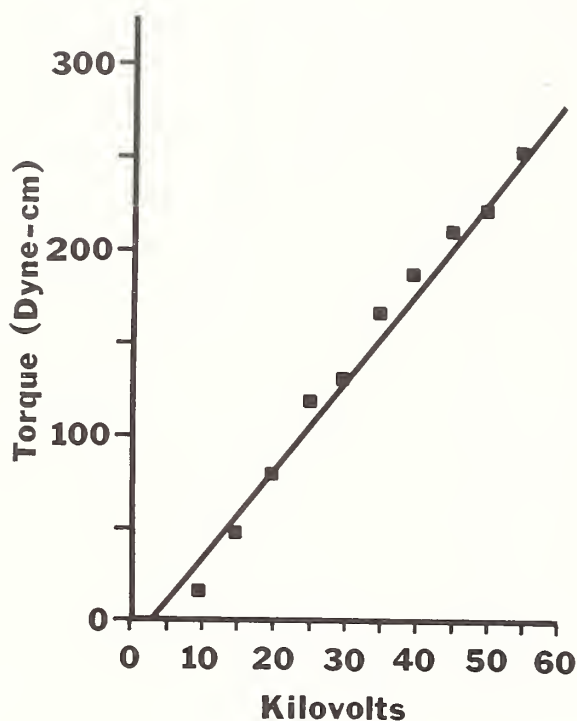


Figure 2. — Torque on fiber aggregate of constant charge.

The dielectric constant of cotton fiber was measured by a novel method based on the Faraday method for measuring magnetic susceptibility.

Generally, the dielectric constant of cotton is measured by the A.C. bridge technique used for measuring capacitance. Reliable data are difficult to obtain by this procedure since it is difficult to determine the packing volume of cotton between the plates of the capacitor. The modified Faraday method is independent of the shape of the sample. In a non-uniform field every dielectric material has a force acting on it given by

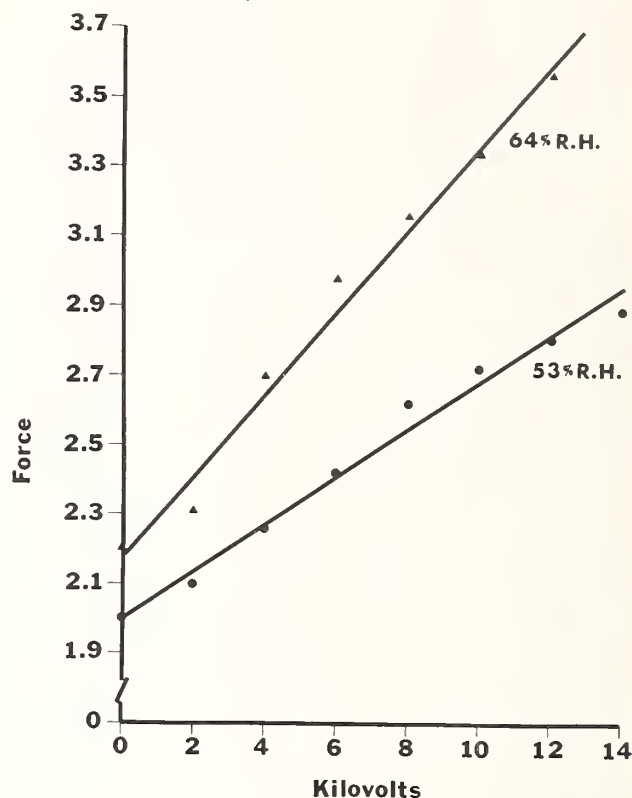


Figure 3. — Force in dynes on individual fibers with constant charge.

With the special geometry developed by Faraday, force on the fiber samples can be plotted versus the square of the voltage giving a straight line fit. The slope of this curve is proportional to the value of the dielectric constant of the cotton fibers. The results obtained by this method agree favorably with the dielectric constant values reported by other researchers.

Although this program was conducted in one set of environmental conditions, it is felt that the information gained will be of great value to further research in the development of a new textile processing system.

# TOTAL OXYGEN DEMAND OF VARIOUS WARP SIZE FORMULATIONS

by

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The total oxygen demand (TOD) of waste water obtained from the desizing of cotton yarns and fabrics treated with various polymers and sizing agents was determined and compared. The initial objective of the research with polymer size formulations was to improve weaving efficiency, durable-press properties, and reduce pollution potential of warp sizes. Some formulations analyzed included those containing carboxymethylcellulose, polyvinyl alcohol, and starch, either alone or in combination with a low level (2.7 percent) of dimethylol dihydroxyethyleneurea (DMDHEU). Other formulations investigated contained permanent warp sizes such as polyacrylates and polyurethanes. These formulations were also used in combination with a low level of DMDHEU. In addition, the permanent sizes were used in combination with carboxymethylcellulose and polyvinyl alcohol to increase weaving efficiency.

The desizing of the warp sized yarns and fabrics to obtain waste water samples was conducted by placing a 50 gram sample of yarn or fabric in 1,500 grams of water containing 0.1 percent of an alkylaryl polyether sulfate wetting agent and boiling for 30 minutes. In cases where starch was the sizing agent, 0.3 percent of an enzyme was added and the bath was held at 190° F for 30 minutes.

The most widely used methods for analyzing waste water in pollution control are the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) methods. The BOD method of analysis is used to determine the amount of oxygen consumed during biological oxidation, but the method has a distinct disadvantage in that 5 days are required to conduct the determination. Furthermore, any oxygen consumed after the 5-day period is not accounted for. The COD method of analysis offers a means of determining the amount of oxygen required to convert organic matter to carbon dioxide and water through chemical oxidation. The major advantage of this method is the short time (3 hours) required for the analysis. However, this method does not differentiate between biodegradable and biochemically inert organic material.

Another method of analysis is the total

oxygen demand (TOD). This method is used to determine the amount of oxygen required to convert organic or inorganic materials to their stable oxides by reaction at temperatures in the vicinity of 900° C. Although the method is not useful in determining the biodegradability of a substance and is similar to the COD method of analysis, the major advantage of this method is that only 3 minutes is required for each determination. The TOD method of analysis is not only useful in determining the pollutorial strength of waste, but also in determining the effects of variation in warp size formulations. The most widely used warp sizing agents in the textile industry are carboxymethylcellulose, polyvinyl alcohol and starch. The TOD of waste water from warp yarns sized with these materials was determined. The waste from 12.6 percent starch sized yarn had a TOD value that was 48 percent greater than that for yarn sized with 4 percent carboxymethylcellulose and 58 percent greater than that for 4 percent polyvinyl alcohol. Substantially lower TOD values were obtained by incorporating 2.7 percent DMDHEU in the sizing formulations and then curing the yarns for 10 minutes at 320° F. before desizing. After curing the TOD values were reduced by 66 percent for starch, 48 percent for polyvinyl alcohol and 34 percent for carboxymethylcellulose waste. In this case the TOD of the starch sized waste was approximately the same as that of the polyvinyl alcohol waste sample. However, the TOD of the carboxymethylcellulose was 30 to 35 percent greater than that of the starch and polyvinyl alcohol sized waste.

Carboxymethylcellulose and polyvinyl alcohol were also used in combination with polyacrylate and polyurethane permanent sizing agents. The main reason for combining these sizing agents in a single formulation was to improve the weaving efficiency of polymer-treated yarns. An unusually high amount of shedding and buildup of polymer on the loom occurred when 12 percent of the polymers were used. This problem was eliminated by reducing the concentration of the permanent polymer size in the bath to 8 percent and substituting 4 percent of carboxymethylcellulose or polyvinyl



alcohol. The TOD value for the carboxymethylcellulose-polyacrylate waste sample obtained from uncured yarn was approximately 13 percent greater than that for the carboxymethylcellulose waste sample alone. A similar increase was also obtained for the carboxymethylcellulose-polyurethane combination. However, after curing the carboxymethylcellulose-polyacrylate yarn there was a 17 percent reduction in TOD compared with the carboxymethylcellulose waste control. The carboxymethylcellulose-polyurethane waste sample had a slightly higher value than the carboxymethylcellulose waste control. In all cases, the TOD values of waste water obtained after curing were 32 to 50 percent lower than those of the uncured samples and the carboxymethylcellulose-polyacrylate size showed the greatest reduction in TOD.

Waste water samples obtained from yarn sized with polyvinyl alcohol, polyvinyl alcohol-polyacrylate, and polyvinyl alcohol-polyurethane had TOD values that were slightly higher than the corresponding treatments with carboxymethylcellulose. However, upon curing these yarns, the TOD values of the waste water samples were 44 to 61 percent lower than those for the uncured samples. Furthermore, the TOD values of the waste from the cured polyvinyl alcohol and the polyvinyl alcohol-polymer series ranged from 7.5 to 26 percent lower than those obtained from the corresponding and carboxymethylcellulose series. The greatest reduction in TOD was obtained with the polyvinyl alcohol-polyacrylate combination.

An analysis of TOD values of waste water obtained from unsized raw yarn showed that even without warp sizing agent, the sample had a TOD value of 1150 mg./l. If the water contained 0.1 percent of an alkylaryl polyether sulfate wetting agent only, the TOD value was 520 mg./l. This means that the raw yarn was responsible for approximately 630 mg./l of the total TOD. The data indicate that in cases where DMDHEU is included in the warp size formulations and these sized yarns are cured, the raw yarn and wetting agent may account for 42 to 60 percent of the total TOD. These results suggest that the type of wetting agent used should be evaluated for pollution control. Of course, other factors such as efficiency of wetting and biodegradability also have to be taken into account.

The TOD of waste water obtained from

fabrics that were warp sized was also determined. A comparison of TOD values obtained from the waste water from yarn and fabric indicated that the TOD values of waste water from fabric sized with carboxymethylcellulose and starch were 39 and 36 percent, respectively, lower than those from yarn. The TOD value for polyvinyl alcohol warp-sized fabric was 17 percent lower. After crosslinking the fabrics that were warp sized with 2.7 percent DMDHEU in the formulation, the TOD of the fabric waste water from carboxymethylcellulose samples was 41 percent lower than the comparable yarn sample. Both the polyvinyl alcohol and starch fabric water wastes were approximately 20 percent lower than their respective yarn samples. A comparison of carboxymethylcellulose-polymer and polyvinyl alcohol-polymer warp-sized fabric and yarn-water wastes revealed that the TOD of the fabric-water wastes were substantially lower than the values for yarn in cases where the soluble sizes were combined with polyacrylate. Where polyurethane was used in combination with the soluble sizes, the improvement was much less pronounced. Curing the carboxymethylcellulose-polymer size in combination with DMDHEU led to a 21 and 34 percent reduction in TOD compared with the water wastes from yarn sized with polyacrylate and polyurethane. After curing the fabric containing polyvinyl alcohol-polymer size in combination with DMDHEU, the TOD for the fabric waste water containing polyacrylate was reduced only 8 percent when compared with that from yarn whereas the reduction with the polyurethane was 29 percent. The lower decrease in TOD in the case of polyacrylate for the fabric-waste water was mainly due to the low TOD of the yarn waste water whereas in the case of polyurethane, the TOD from the yarn waste water was 42 percent higher than the waste water from yarn sized with the polyacrylate. The data show that it is possible to insolubilize a water soluble polymer by incorporating a small amount of crosslinking agent such as DMDHEU in a warp sizing formulation. By combining water soluble sizing agents with permanent warp sizing agents, weaving is increased. In addition, the durable press properties of the resulting fabric are enhanced. Finally, the total amount of sizing agent that is removed from the fabric during the desizing operation can be substantially reduced.

# CHEMICAL FINISHING OF COTTON YARNS FOR IMPROVED KNITTABILITY

(A Preliminary Report)

by

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(Presented by William G. Wolfgang)

## INTRODUCTION

Although cotton yarns have been used successfully in knitting for many years, the principle uses have been with the coarser counts and in the heavier, lower priced constructions. The principal limiting factors in the use of the finer counts, the lighter, fine gage knitted constructions are the tendency of such yarns to lint excessively, the lack of strength and uniformity of strength, and the lack of diameter uniformity. The purpose of this research was to seek methods, through the chemical finishing of the yarns, which would minimize these defects and make cotton yarns available for the finer gage, lighter knitted fabric constructions.

Although early in the project it was felt that some improvement in diameter uniformity of cotton yarns could be accomplished by die coating the yarn with a filmforming finish, the results of the method have been disappointing. Therefore, we concluded that the necessary improvements in yarn diameter must be accomplished during the yarn manufacturing process. This report will concern itself mainly with the methods and techniques which have been investigated to reduce the linting tendency of the cotton yarns and to improve the strength and uniformity of strength.

The work has been divided into two main phases:

- (1) the screening of various potential finishes and application techniques followed by the optimization of the best of these and
- (2) the use of the best technique in a semi-plant trial. The first phase will be covered in this paper.

## INITIAL SCREENING

Compounds were selected for initial screening to provide a wide range of chemical types. The materials used, the screening application and the materials selected for further evaluation are shown in table 1.

Many of these materials were found to either do nothing to the yarn properties or to indeed have a dilatorious effect. Hence the remainder of the effect was concentrated on developing optimum application techniques and concentrations for the materials indicated with an asterisk in table 1.

## APPLICATION METHODS

The initial screening was first carried out by using a die coating method on 30/1 carded, bleached cotton yarn. On the materials selected for further evaluation the method produced rather uniform coatings and yarn strength was also improved. However, there was little or no improvement in overall yarn diameter uniformity and the process proved to run rather slowly. A pad method was then tried as an alternative. Initial test run by using the same treating materials at the same concentrations as were previously run with the die method, indicated that similar or improved results could be obtained by the pad method and that higher production speeds could be obtained. All further studies used the pad method. The details of the pad method are as follows:

- (a) The method treats a single end of yarn in a continuous fashion.
- (b) The yarn is passed through a single dip in the treating solution followed by a single nip through the pad rolls.
- (c) The pad rolls are 2 inches in diameter with a 2 inch wide face a load of 40 pounds is applied to each of both ends of the top roll axle.
- (d) The yarn is dried by passing between two 4,000 watt, quartz tub infrared heaters which are 6 feet long.
- (e) The yarn is wound on a 3 inch cone.

## NYLON APPLICATION BY INTERFACIAL POLYMERIZATION

Inasmuch as the application of a nylon resin from a solvent system proved ineffective, and it was felt that the application of such a resin should show some beneficial results, an experiment was made to make the application by an interfacial polymerization procedure. The pad previously described was used for the application using both of the roll pairs with which it was equipped.

The yarn was first entered into a bath containing a 6 percent by weight aqueous solution of hexamethylene diamine, squeezed and then entered into a bath containing a 5 percent by weight solution of sebacyl chloride in perchloroethylene, again squeezed and dried as in the usual pad technique.



A good coating was obtained on the yarn and the yarn properties seemed to be improved. Reversing the order applying the treating chemi-

cals did not give as good a coating. The optimization procedure was carried out on the previously described order of application.

Table 1: — Materials Initially Screened as Potential Finishes for Cotton Knitting Yarns

Material	Trade Name	Application conc. & solvent	Further evaluation
Carboxymethyl cellulose	CMC	3 pct. aqueous	*
Methylcellulose	Methocell MC	2 pct. aqueous	*
Hydroxypropylcellulose	Klucel	20 pct. ethanol	*
Ester of vinylmethyl ether and maleic anhydride	Apertan N	25 pct. aqueous	
Polyethylene	Trisco Polyeen N	30 pct. aqueous emulsion	
Natural rubber		20 pct. toluene aqueous	
Polyethylene oxide	Carbowax 600 & 1500		
Polyethylene-vinylacetate copolymer	Elvax 40	40 pct. perchloro-ethylene	*
Butadiene-acrylonitrile copolymer	Hycar 1571	41 pct. latex	
Resin-petroleum wax	Ingra-Tex	36 pct. aqueous emulsion	
Paraffin wax		20 pct. mineral spirits	
Vinyl latex	Geon 576		
Polyacrylic material	Acranyl 25	6 pct. ethanol	
Polyisobutylmethacrylate	Elvacite 2045	20 pct. mineral spirits	
Nylon resin	Elvanmide	40 pct. formic acid	
Nylon by interfacial Polymerization	Resin APX	60 pct. emulsion	
Polyvinylacetate	Soloid	10 pct. mineral spirits	*

### OPTIMIZATION EXPERIMENTS

The optimization procedure consisted of the pad application of the several agents selected for further study, at several bath concentration levels. The yarns so processed were then tested for tensile properties by both the CRL and CRT machines, loop strength and frictional properties. The friction properties were determined by using the AtLab tester with the metal friction bars replaced by a fine gage latch knitting needle. The running speed was 600 cm./min. Observations were also made of the tendency of the yarn to lint during this test. The results of these observations indicated that a significant improvement in the tendency of the yarn to lose fiber was made by all of the treatments as compared with the untreated control yarn. There was also no observed tendency for the treated yarns to shed the coating material.

Since the program was aimed at improving the qualities of fine cotton yarns the optimiza-

tion procedures were carried out on a 70/1 combed cotton yarn with 35 TPI Z twist.

The initial experiments using the cellulose ethers produced yarns with an undesirable increase in stiffness. To overcome this defect a softener (Craemoyl) was added to these materials at a level of 25 percent of the weight of the cellulose ether.

The application levels and the results of the above physical tests are shown in table 2. If the combination of toughness and loop strength is used at the criterion, the following levels are optimum for each of the treatments:

Nylon 1.25 percent HMD/1.5 percent SBC1  
CMC 1 percent + 0.25 percent Creamoyl  
Methocel 1 percent + 0.25 percent Creamoyl  
Klucel from ethanol 1 percent + 0.25 percent Creamoyl  
Klucel from water 1.25 percent  
Elvax 1.67 percent  
Soloid 1 percent

The use of the same criterion Elvax at the 1.67 percent level seems to be the optimum treat-

ment closely followed by Klucel from water at the 1.25 percent level.

Table 2: — Comparative Properties of Treated Yarns for Optimization

Treatment	Break (g)	C.V. (pct.)	Elongation	C.V. (pct.)	Toughness	C.V. (pct.)	Stiffness	Loop grams	Strength C.V.(pct.)	Friction in/out
Control	134.2	16.5	5.8	12.4	390.8	21.6	40.0	203.3	11.4	1.9
Nylon IFP										
6 pct. HMD/5 pct. SBCI	133.9	17.9	2.75	18.2	188.5	34.3	63.4	250.7	22.5	4.0
3 pct. HMD/2.5 pct. SBCI	163.0	11.9	3.21	16.8	265.3	25.0	75.2	202.0	15.0	4.0
1.5 pct. HMD/1.25 pct. SBCI	166.6	13.6	3.46	22.8	289.5	35.0	55.6	204.8	12.0	2.1
CMC+soft										
2 pct.	191.2	21.7	3.3	28.2	331.6	40.6	77.0	228.0	11.3	2.1
1 pct.	191.2	14.7	3.73	12.6	361.6	24.8	66.8	275.2	19.8	1.9
0.5 pct.	172.8	15.3	3.88	13.4	335.8	21.9	50.4	193.6	7.4	1.9
0.25 pct.										
Klucel+soft										
/ethanol										
5 pct.	154.0	15.1	3.6	18.6	283.7	31.4	34.0	186.0	12.8	1.9
2 pct.	144.4	17.0	4.22	19.2	313.1	32.9	30.4	181.6	18.6	2.1
1 pct.	152.0	17.9	4.36	16.7	339.4	31.7	30.4	227.3	11.2	1.9
Klucel (NS)										
/ethanol										
5 pct.	161.6	16.4	3.65	18.6	301.4	32.6	31.6	186.7	14.9	2.0
2 pct.	151.6	10.6	4.8	12.7	366.4	20.7	28.4	256.7	11.5	1.9
Klucel										
/water										
5 pct.	172.6	12.2	3.48	14.4	304.3	23.5	38	321.6	7.09	2.1
2.5 pct.	186.8	14.7	3.09	17.8	295.8	31.8	48	346.0	6.04	1.9
0.25 pct.	172.8	14.0	3.4	17.3	299.6	29.6	45.2	342.0	8.6	1.9
Methocel+soft										
2 pct.	145.7	16.0	3.36	17.3	247.3	28.0	45.6	212.8	11.2	2.0
1 pct.	162.0	17.4	2.89	22.1	242.3	38.8	46.1	270.0	9.0	2.0
0.5 pct.	152.8	15.0	2.97	22.2	234.1	37.8	41.4	194.4	12.9	1.9
Elvax										
10 pct.	155.4	16.7	3.66	16.4	289.8	31.1	34.0	250.4	8.7	2.9
5 pct.	158.7	16.1	4.46	17.9	363.2	33.4	30.4	261.3	10.0	1.9
1.67 pct.	165.5	10.9	4.71	16.7	393.2	23.2	30.7	292.0	10.6	2.0
Soloid										
2 pct.	160.5	14.0	4.89	18.2	395.6	24.9	38.2	256.0	8.5	2.0
1 pct.	160.0	11.8	5.49	11.8	444.7	23.5	42.0	248.8	8.5	2.0
0.5 pct.	161.0	8.3	5.08	11.4	412.3	19.0	36	247.0	8.6	2.0

In all of the treated yarns there seems to be high degree of correlation between the breaking strength and the breaking extension which is not found in the control yarn. The coefficients of correlation of breaking strength to breaking extension range from 0.68 to 0.95 for the treated yarns as compared to 0.26 for the control yarn. This leads us to believe that there is a different breaking mechanism for the treated yarns than in the control yarn.

Knitting trials on the 70/1 yarns were disappointing. Low strength of the base yarn and the increase in strength due to the treat-

ments were insufficient to allow knitting a tight construction. To determine the reason for the poor knitting performance, the optimum treatments derived for the 70/1 yarn were applied to a 55/1 cotton yarn which had a twist multiplier of 3. These yarns were subjected to the same battery of tensils and loop strength tests with the results as shown in table 3.

The table shows that the results of the treatments are quite similar to those obtained on the 70/1 yarn and that the same treatments represent the optimum treatments.

Table 3. The properties of 55/1 cotton yarns treated with the best of the agents & concentrations shown in table 2

Treatment	Tensile (grams)	C.V.	Elongation (percent)	C.V.	Toughness	C.V.	Loop (grams)	Strength C.V.
Control	179.6	12.2	6.69	7.2	605.0	17.2	334.4	11.4
Elvax 1.67 pct.	197.6	6.0	6.4	4.8	633.6	10.1	368.0	8.7
Klucel 1.25 pct. from ethanol	194.7	8.4	6.8	8.2	666.0	15.8	416.0	8.2
Klucel 1.25 pct. from water	202.9	8.4	6.3	10.6	639.4	18.0	398.4	18.4
CMC 1 pct.	198.2	5.9	5.3	7.5	528.2	12.5	386.0	6.0
Methocel 1 pct.	190.0	8.1	5.3	7.5	509.0	13.4	374.0	4.9

### SUMMARY

The treatment of 100 percent cotton knitting yarns can result in an increase in strength, increase in strength uniformity, increase in loop strength and loop strength uniformity. These same treatments will also decrease the linting tendency of the yarns during passage over the knitting needle. The treatments that produce the most desirable results are:

- (1) A 1.67 percent by weight solution of Elvax in perchloroethylene
- (2) A 1.25 percent by weight solution of

Klucel L from either a water solution or a 95 percent ethanol solution, with or without the addition of 0.25 percent softener.

The application technique is by single end padding although there seems to be no reason why the same technique cannot be applied to warps. The Elvax treatment is easily removed by cleaning in perchloroethylene and the Klucel treatment can be easily removed by a cold scour with water or with 95 percent ethanol.

## CHEMICAL PROCESSING OF COMMERCIAL TYPE FABRICS FROM DISCOUNT COTTONS

by

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### ABSTRACT

Direct and reactive dyeing tests were examined as a means of monitoring efficiency of blending cottons differing widely in maturity. If it is desired to determine whether maturity differences will cause difficulties in dyeing with dyes and processes which do not mask such differences, the Goldthwait-Smith-Barnett (GSB) (7) test and the Textile Research Center (TRC) test, newly developed, are useful. The TRC test has been found superior to the GSB test in several respects. If on the other hand, it is desired to determine whether maturity differences will cause difficulties in dyeing with dyes

and processes which do mask maturity differences, the GSB and TRC tests are not indicated, rather reactive dyeing tests are indicated.

Dyeing tests indicated that blending through the second drawing stage could not be described as having produced an absolutely uniform long-range axial distribution of high-and low-maturity cotton. However, the blend was good enough that 500 yard lengths of a 3/2 twill, a bedford cord, a bark cloth, and a terry toweling were dyed to uniform shades acceptable in terms of end to end and side to center levelness, neppy unlevelness, and levelness along discrete yarn lines or segments thereof.



A dyeing test to be used on staple samples was developed to allow prediction of success in level reactive dyeings of non-exhaustion processes on fabrics made from blends of high and low micronaire cotton.

## INTRODUCTION

The supply-demand situation for cotton has changed significantly during the past several years. Not only technological advances and economic pressures in the agribusiness and textile industries, but also social and cultural forces have contributed to this. The latter have produced a new popularity for cotton as a natural comfort-fiber (13).

Over the last five decades, it had become almost an unchangeable principle that blends of cottons having widely divergent micronaire, or other maturity-related values, would cause serious difficulties in the mechanical operations of yarn formation and dyeing yarn or fabric to union shades (1, 2, 4-8, 19-23). Difficulties in both process efficiency and product quality were cited.

It is proposed that difficulties in yarn manufacturing and dyeing, due to blends of cottons having widely divergent micronaire values, were more real in earlier times than they have to be now. Improved fiber blending operations that have evolved since the late 1950's, that is, during the polyester/cotton blend era, are now widespread. Furthermore, dyeing technology has advanced dramatically since the early 1940's. Limitations on cotton fiber blends, based on yarn manufacturing and dyeing difficulties in earlier times, must be reassessed in terms of technology practices in today's yarn mills and dyeing/finishing plants. Thus it is imperative, in a tight supply-demand condition that may not be short-lived, to examine possibilities for more effective, rational use of the various cottons as textile raw materials. A total system mentality must increasingly be acquired.

Some of these factors, as well as others, justified research to demonstrate, for nine standard woven fabrics made from a blend of cotton of micronaire values of 2.9 and below and 5.3 and above, that difficulties in yarn manufacturing and dyeing need not occur. Parts of this research have been already reported (24, 26) and three other reports will appear shortly (14, 15, 25). It was also desired to demonstrate that extremes in grade (color) could be handled without difficulty in yarn manufacturing, bleaching, and dyeing.

## MONITORING BLENDING EFFICIENCY VIA DYEING TECHNIQUES

The design for the mechanical operations of yarn formation, including blending, and the greige fabric construction specifications have

already been described (24-26). Table 1 exhibits the properties of the cotton raw stock. Fourteen bales of cotton of a mean micronaire greater than 5.3 were blended with 14 bales of cotton of mean micronaire less than 2.9 to give an overall mean micronaire value of 3.9.

Table 1. Fiber properties of cottons selected

Function	Number of bales	Micronaire reading	Non-lint content (pct.)	Color grade
Mean	7	5.62	2.46	SLM
CV (pct.)		4.05	24.86	
Mean	7	5.55	2.38	SLM
CV (pct.)		5.43	20.50	
Mean	7	2.69	8.79	LM SP.
CV (pct.)		5.84	18.57	
Mean	7	2.87	7.36	LM LT. SP.
CV (pct.)		3.95	10.35	
G. Mean <sup>1</sup>		3.916	4.83	

<sup>1</sup>Weighted for blended properties to result in a 3.8 to 4.0 micronaire at finisher drawing.

It has become almost axiomatic over the past 50 years that blends of cottons differing widely in micronaire, or other maturity-related values, will cause major difficulties in dyeing yarn or fabric to union shades (1, 2, 4-8, 19-23). In the late 1940's, the Goldthwait-Smith-Barnett (GSB) differential dyeing technique (1, 2, 7, 23) was developed to aid in identifying cotton fiber maturity differences and thereby to allow "selecting cottons for even running and dyeing, for minimizing dyeing defects due to excessive neps, and for avoiding such troubles as may arise from irregular blending of fibers of different dyeing characteristics." (1).

Unlevel dyeings associated with maturity differences may be related to two different types of fiber distribution non-uniformity. Firstly, neps of immature cotton on a fabric field of a uniformly distributed blend of high and low maturity cotton in the yarns can cause an obvious specky differential dyeing (unevenness), the neps usually being dyed to a lesser depth of the same hue. Secondly, a non-uniformly distributed blend of high-and low-maturity cotton in yarn, otherwise nepless, can cause differential dyeing along discrete yarn lines, or segments thereof. Even in a nepless and uniformly distributed blend of high and low maturity cotton in yarns, a skittery, frosty unevenness could result. All these sources of unevenness depend on differing dye uptake, being referred to as differential dyeing (1, 2, 7, 23). This produces a depth difference, usually at a constant hue, which is

large enough to be troublesome, that is, leading to unevenness, but too small to be technically useful as in various differential dyeable natural and synthetic fiber sets recently available (12).

The major contributor to levelness difficulties in dyeing yarns or fabrics containing immature cotton has been identified as neps, which are a short range non-uniformity being wholly or largely composed of immature cotton (8). However, in fabrics containing as much low micronaire cotton as the ones in this work, it would be expected that, even in nepless fabrics<sup>1</sup>, a uniform long range distribution of the two cotton maturities both radially and axially in the yarn would become more important. In fact, it was recognized at the outset of this work that a good radial and axial blend could be an important condition for obtaining successful (level) piece dyeings to union shades. It is logical that, for two differently dyeing fiber types, a uniform blend will produce the minimum concentration of either of the fibers at all locations. In this situation, the eye might detect a frostiness or skitteriness in the dyed fabric, but not a speckiness due to neps, or an unevenness along discrete yarn lines or segments thereof.

Since such short and long range non-uniformities result from non-optimum mechanical operations in yarn manufacturing, it was important to monitor blending efficiency. This was done not only by micronaire measurements but also by dyeing tests which should be more relevant. The dyeings were of three types:

- (1) The GSB differential direct dyeing technique [ASTM D 1464-63] (2),
- (2) The TRC direct dyeing technique developed for this work, and
- (3) A yellow reactive dyeing.

The GSB differential dyeing test uses a binary direct dye combination (Chlorantine Fast Green BLL and Diphenyl Fast Red 5BL). As a result of the dyeing<sup>2</sup>, immature cotton fibers are dyed more or less green, and mature fibers are dyed more or less red. The GSB test utilizes only visual assessment and reports only qualitative, comparative rankings. One serious difficulty with the GSB test is connected with the gray component, resulting from subtractive mixing of red and green from correspondingly colored fibers. It is rare to find a sample of ginned cotton which has anything but a mixture of maturities, thus one generally obtains GSB

dyeings on staple samples which range from greenish-gray to reddish-gray. The gray component is often large and always troublesome, since even long experienced color matchers have difficulty in correctly (visually) assigning the true gray concentration to lightness-darkness rather than to saturation. Thus, it is well that the ASTM test (2) does not propose any scheme of visually assessed rankings with reference to an absolute scale. Koch (16, 17), however, used a 0 to 5 scale for reporting GSB results, 5 representing the most mature and 0, the most immature. A comparison by Koch in 1971 (16, 17) of the GSB, causticaire, and micronaire tests to microscopically determined maturity, showed that the GSB test correlates worst. This may be chiefly due to the gray component difficulty and its effect on the visual ranking procedure. It is quite clear, however, that the GSB test does visually emphasize maturity differences and very greatly so. It was used in this work since it is a very real part of the common currency of maturity testing. It was desired to see how it would perform when an attempt was made to quantify its results on various textile protostructural and structural stages of the project, using reflectance spectrophotometry which to our knowledge had not been attempted.

In order to obtain numerical results, free from the gray component difficulty, a modified GSB test, referred to as the TRC (Textile Research Center) test was developed. More detail on this is reported elsewhere (15). Briefly, it is based on the use of only one of the GSB dyes, the larger molecular weight green dye: it proposes that the rate of absorption of this dye should be maturity-dependent, that is, the rate of dyeing of immature cotton should be much faster than that for mature cotton. An important consequence of the TRC test is that maturity differences will be related only to color saturation, that is, depth of shade or dye concentration, not to saturation, hue, and lightness as in the case with the GSB test. One might say that two dyes in the GSB test is one too many. The TRC test, therefore, has the potential advantages, at least, of (a) less confusing visual evaluation of color differences, (b) more rational instrumental quantification of color differences, and (c) a simpler dyeing procedure since the boiling water rinse of the GSB test is omitted.

<sup>1</sup>It is important to note that cotton sticking to metallic or rubber rolls in the mechanical operations of yarn formation was observed at no time in this work. Close surveillance for this phenomenon was maintained. From statements in the literature (20), stickiness due to the low micronaire cotton would have been expected. In view of the large percentage of low micronaire cotton used, low process efficiency and a very high nep count could have been expected (20) on this basis. Table 4 of reference 25 indicates, however, that the latter did not happen.

<sup>2</sup>The GSB test dyeing method is readily accessible (2) and it is not repeated here.



The reactive yellow dyeings were run according to conventional exhaustion technique and were included since the direct dyes of the GSB and TRC tests may in fact overemphasize maturity differences in relation to what is real and practical in current dyeing technology.

Figures 1, 2, 3, and 4 show the correlation we have obtained between microscopically determined maturity and micronaire, GSB, TRC, and reactive yellow dyeing tests, respectively. It is emphasized not only that these correlations result from a set of similar variety cottons over the whole maturity range but also that the dyeing tests involved quantitative instrumental evaluation. Table 2 compares our results to those of Koch. It is obvious that the GSB test correlates very well with maturity if the results are quantitatively handled. The TRC and reactive yellow dyeing tests give the same order of correlation with maturity. It is indicated that any of the three dyeing tests would be useful in monitoring maturity differences. They all have the advantage over micronaire values of yielding visually perceptible differences and greater sensitivity to differences in maturity.

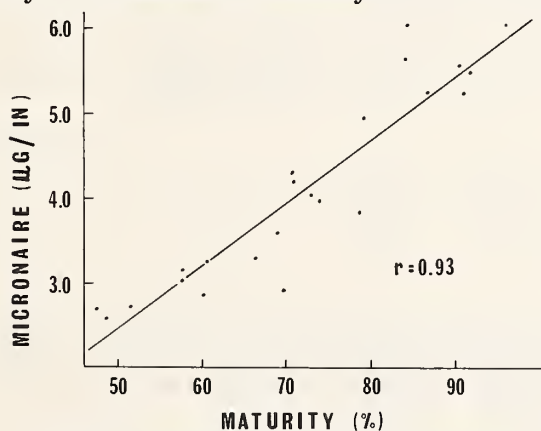


Figure 1. Micronaire dependence of maturity

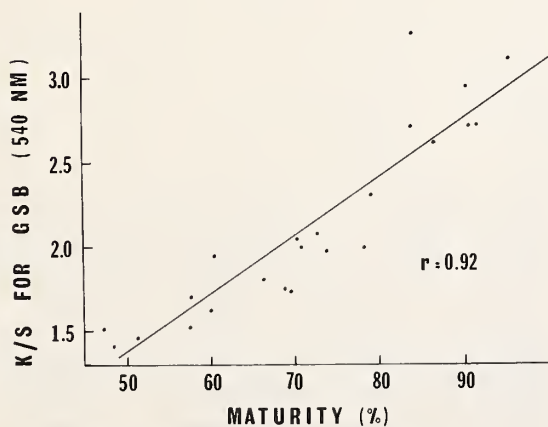


Figure 2. Dependence of  $K/S_{540nm}$  for GSB dyeing test on maturity

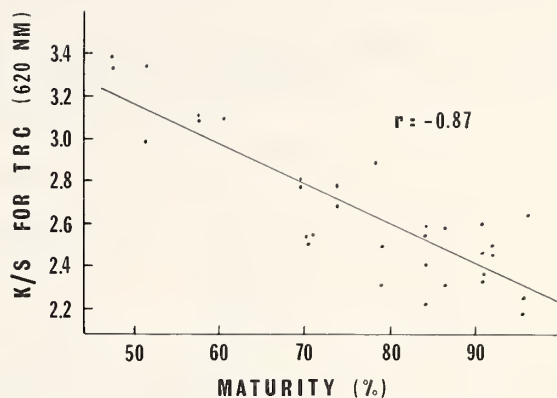


Figure 3. Dependence of  $K/S_{620nm}$  for TRC dyeing test on maturity

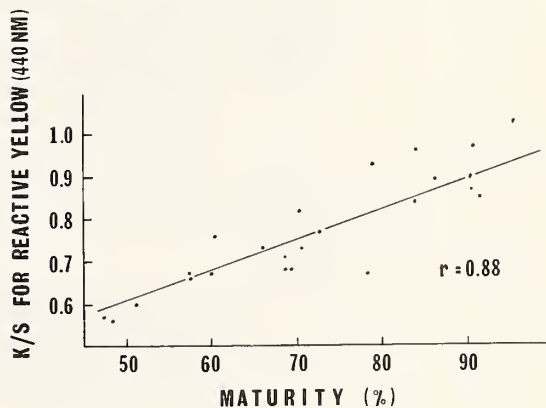


Figure 4. Dependence of  $K/S_{440nm}$  for reactive yellow dyeing test on maturity

For the research at hand, it is only possible to evaluate the effect on dyeing of blending the two widely differing micronaire populations used here (see table 1). The mean micronaire values of the low micronaire population and the high micronaire population are separated by about 2.8 micronaire units, which is a large separation. In the work to monitor blending by dyeing tests, a high micronaire set of 28 unblended staple samples which came from 28 half-bales of cotton with a mean micronaire value greater than 5.3 was used as well as a low micronaire set of 28 unblended staple samples which came from 28 half-bales of cotton with a mean micronaire value less than 2.9.

Table 3 shows reflectance colorimetric data related to determination of blending efficiency via dyeing techniques. The colorimetric parameter  $K/S$  has its usual significance of direct proportionality to depth of shade (3). Comparison of determined  $K/S$  values for (blended)

silver to values calculated on the basis of the actual blend ratio indicates better agreement for

the TRC dyeing test.

**Table 2. Correlation of rapid maturity test methods to microscopically determined maturity**

Rapid test method	Microscopically determined maturity Correlation coefficient (r)	
	Koch	Texas Tech
Causticaire	0.83	----
Micronaire	.77	0.93
GSB (visual qualitative ranking on 0-5 scale)	.68	----
GSB (instrumental quantitative)	----	.92
TRC (instrumental quantitative)	----	-.87
Reactive (instrumental quantitative) yellow	----	.88

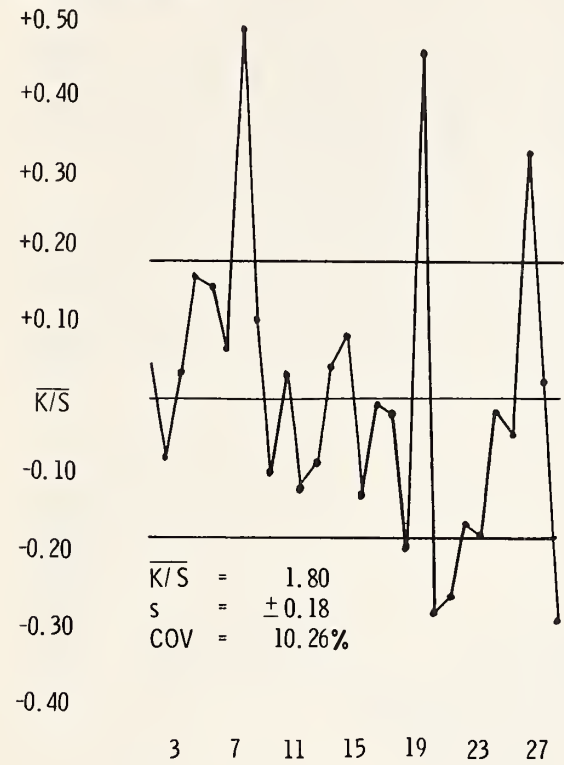
**Table 3. Dyeing tests in monitoring blending efficiency**

Test		$\overline{K/S}$	Calculated
GSB dyeing on:			
A.1	Low micronaire unblended staple	1.80	2.39
A.2	2nd drawing sliver from unblended staple	2.18	
A.3	High micronaire unblended staple	2.83	
TRC dyeing on:			
B.1	High micronaire unblended staple	2.36	2.74
B.2	2nd drawing sliver from unblended staple	2.69	
B.3	Low micronaire unblended staple	3.03	
0.2	percent intracon golden yellow		
F2R-A dyeing on:			
C.1	Low micronaire unblended staple	.76	.94
C.2	2nd drawing sliver from blended staple	.88	
C.3	High micronaire unblended staple	1.07	

The  $\overline{K/S}$  values in table 3 were derived from plots like those in figures 5 and 6. Figure 5 exhibits the variability of cotton maturity as monitored by  $\overline{K/S}$  from GSB540 dyeings throughout the low micronaire set of staple samples from 28 half-bales. Figure 6 shows the same parameter throughout the high micronaire set. It is, therefore, obvious that within the separate sets of 28 low, or 28 high micronaire unblended staple samples, variability as moni-

tored by GSB540 was considerable. It was found that the TRC test identified similar variability, but the reactive yellow tended to mask variability. GSB and TRC direct dyeing tests do effectively monitor (emphasize) large and small maturity differences, if it is desired to determine whether maturity differences will cause difficulties in dyeing with dyes and processes which do not mask or cover maturity differences. However, reactive dyeing tests would not be

very effective in that regard — they would be relevantly used to determine whether maturity differences will cause difficulties when dyeing with dyes and processes which mask or cover such differences.



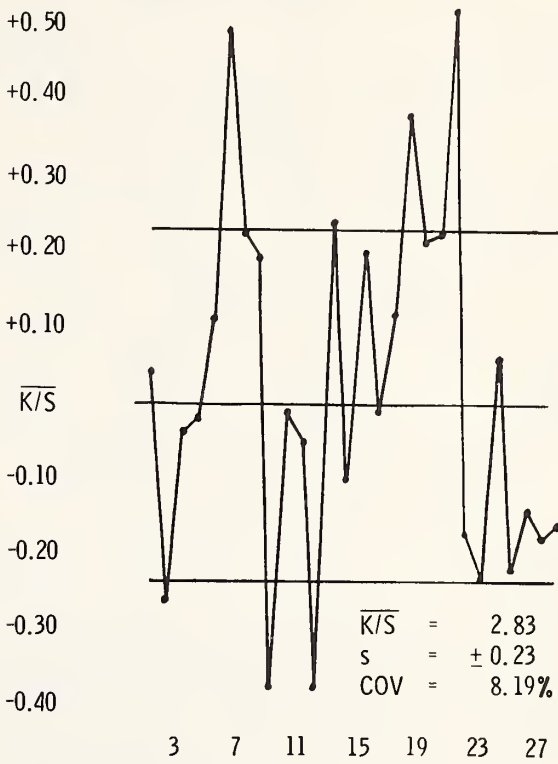
LOW MICRONAIRE SET FROM 28 HALF-BALES

Figure 5. Variability in maturity shown by GSB test in a set of samples from 28 half-bales of low micronaire cotton

It is obvious that variability monitored by dyeing tests exists within the set of either 28 low or 28 high micronaire unblended staple samples, however, it is not as large in the sliver. This demonstrates not only a very sensitive test for maturity but also that the biological materials with which we are dealing are not subject to narrow quality control limits. That is to say, a certain and larger amount of variability should be expected and is shown to occur that would be allowed in industrially manufactured materials. Therefore, blending of high efficiency is all the more imperative.

Figure 7 exhibits a sequential examination of second drawing sliver at 74 points by the TRC dyeing test. Although it is not possible, at this time, to accurately draw limit lines of just perceptible color difference, it is known that there is sufficient color variation to definitely state that blending in this project could not be

described as having produced an absolutely uniform long range axial distribution of high and low maturity cotton. It is realized that the variability within both the high and low micronaire staple sets contributes to the variability apparent in the sliver.



HIGH MICRONAIRE SET FROM 28 HALF-BALES

Figure 6. Variability in maturity shown by GSB test in a set of samples from 28 half-bales of high micronaire cotton

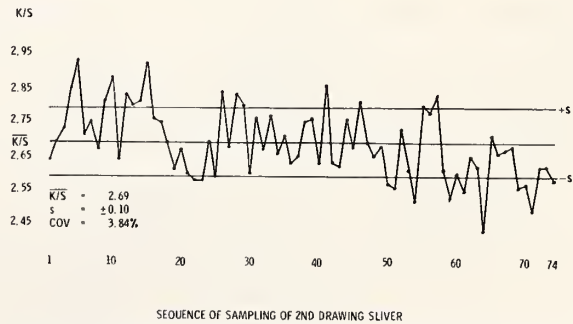


Figure 7. Sequential examination of 2nd drawing sliver at 74 points by the TRC dyeing test

Considering one approach to statistical evaluation of the data on the staple and sliver, one



population was 28 samples of high micronaire staple, a second was 28 samples of low micronaire staple, and a third was 74 samples of second drawing sliver from blended staple. Statistical evaluation of  $\overline{K/S}$  values is found in table 4.

Table 4. Evaluation of  $\overline{K/S}$  data

Dyeing test	$\overline{K/S}$	s	CV (pct.)
<b>Low micronaire staple set</b>			
Yellow reactive	0.76	$\pm 0.04$	5.57
GSB <sub>540</sub>	1.80	$\pm .19$	10.26
TRC <sub>620</sub>	3.03	$\pm .24$	8.02
<b>High micronaire staple set</b>			
Yellow reactive	1.07	$\pm 0.06$	6.01
GSB <sub>540</sub>	2.83	$\pm .23$	8.19
TRC <sub>620</sub>	2.36	$\pm .24$	10.29
<b>2nd drawing sliver from blended staple</b>			
Yellow reactive	0.88	$\pm 0.04$	4.11
GSB <sub>540</sub>	2.18	$\pm .18$	8.09
TRC <sub>620</sub>	2.69	$\pm .10$	3.84

The mean ( $\overline{K/S}$ ) is shown for each dyeing test on each different substrate. The standard deviation(s) is about the same in each set for the reactive dyeing. It is about the same for the GSB and TRC direct dyeings for high-and low-micronaire staple through higher, while s of the TRC test on sliver is significantly lower than s of the GSB test.

The coefficient of variation [CV, percent] expresses the dispersion within the population. The dyeing tests have COVs related as follows:

sliver: TRC<yellow reactive<GSB

low micronaire staple: yellow reactive<TRC<GSB

high micronaire staple: yellow reactive<GSB<TRC.

Therefore, it is shown that as dispersion (CV) decreases (that is, high micronaire staple > low micronaire staple > sliver, so does the dispersion of the TRC test.

Table 5 outlines work on the translation of staple from each of the 14 low micronaire bales and each of the 14 high micronaire bales separately into yarn and then into 3-inch bands in a single jersey knit. It was desired to determine how the three dyeings on three of these 28-banded knits might show color variability within the low micronaire set of bands and within the high micronaire set of bands, and to compare this with the color variability of the

same three dyeings on the low and high micronaire staple sets. This could give information on how much blending out of the relatively small micronaire variation within the low, and high, micronaire staple sets occurs in processing to yarn. Since quantitative color comparisons between dyed staple samples and dyed knit samples would have to be made, the surface form effect would complicate such comparisons. It was found, however, by visual assessment of band junctions in the banded knits (lines A and B, table 5) that none of the three dyeings on the banded knits allowed the conclusion that the blending in conventional conversion of staple to yarn removed all the maturity variability within the low set, or within the high set. As expected, the GSB and TRC direct dyeings tended to emphasize the small variability between bands of one or the other of the maturity sets more than the reactive dyeing.

Table 5. Outline of work on translation effects

Banded knits	GSB dyeing	TRC dyeing	Intracron golden yellow F2R-A 0.2 percent OWF
A. FAK sock knit with 3 in. yarn bands from unblended staple, sample series inserted once only	X	—	X
B. FAK sock knit with 3 in. yarn bands, each of 14 low micronaire yarn bands adjacent to the other 13, and each of 14 high micronaire yarn bands adjacent to the other 13	X	X	—
C. FAK sock knit with 3 in. bands of yarn taken sequentially during mfg. of yarn from blended staple from 28 bales	X	X	X

Analogously, line C of table 5 outlines work on the translation of blended staple into yarn, 10 samples being taken sequentially throughout the spinning of all yarn in the project. These yarn samples were knitted into a 3-inch band in a single jersey knit. There were small but visually detectable color differences between all the 10

bands, that is, between all 10 yarn samples, irregardless of the dyeing method. However, once again the reactive dyeing was more effective in masking differences.

It is important to emphasize that the above-mentioned reactive dyeing tests were done by exhaustion. It is expected that many of the maturity-related color differences in those cases would disappear if the reactive dyeings were done by a non-exhaustion process. In fact, non-exhaustion reactive dyeings are very successful in covering even large maturity differences.

#### CHEMICAL PROCESSING OF FIVE PROJECT FABRICS

Difficulties in dyeing blends of cotton differing widely in maturity (and the associated GSB test) were more real in the 1940's than in 1972. These difficulties were largely coupled to exhaustion dyeing, and to the direct dye class, which is probably the worst class in emphasizing cotton maturity differences (8). To this day in the minds of some (20), there is still a strong image of major problems in dyeing cotton fabrics containing low micronaire fiber. But they have overly generalized the problem, not recalling that, while exhaustion dyeing of cotton with direct dyes was dominant and with reason the major contributor to this image in the 1940's, direct dyes have now been largely superseded for cotton textiles by dyes giving not only more durable and otherwise attractive dyeings, but also having generally good potential for covering maturity differences.

Limitations on cotton fiber blends due to dyeing difficulties in an earlier era of less well-developed dyeing technology must be re-assessed in terms of changes in that technology. Such limitations are not necessarily valid today and, to be sure, if they were, this project, which

involved piece dyeing of four fabrics, could not have been accorded any reasonable chances of success.

Very significant changes in dyeing of cotton fabrics have, in fact, occurred since the late 1940's. The advent of non-exhaustion dyeing processes (10), dyes which are insensitive to cotton maturity differences (see references 10, 22, and shade cards of most dye manufacturers), and treatments before (6, 10, 22) or after dyeing (9, 11, 18) are the most important in regard to the situation at hand. Mercerization after dyeing (9, 11, 18) is particularly useful where dyes insensitive to maturity differences are not immediately available. Even Goldthwait (8) was able to establish in 1961 in a comprehensive survey of commercially dyed cotton fabrics containing immature cotton in neps that coverage of neps in dyeing was much advanced over the late 1940's. In fact, Goldthwait had to use rather extreme means to identify the neps; they were not visually apparent in the commercially dyed fabrics. This improvement over the 15 or so years before 1961 was ascribed by him to the use of non-exhaustion dyeing processes, non-direct dyes, and pre-mercerization.

Just as steps were taken to optimize blending in order to obtain axial and radial uniformity of the two cotton maturities in the yarn, it was also imperative to design the chemical processing so that maturity differences were not emphasized. Briefly, the principles outlined above were employed, that is, non-exhaustion dyeing processes, non-direct dyes, and pre-mercerization.

Chemical process/operations sequences actually used in the semiworks section of the Chemical Processes Pilot Plant to convert the five griegge project fabrics into 500 yard lengths of finished fabrics are summarized as follows:

#### 3/2 Twill (denim)

brushing and singeing  
desizing  
caustic steaming  
bleaching  
mercerizing  
dyeing  
durable press sensitizing  
sanforizing<sup>1</sup>

#### Bedford Cord

singeing  
desizing  
caustic steaming  
bleaching  
mercerizing  
dyeing  
durable press sensitizing  
sanforizing<sup>1</sup>

#### Bark cloth

desizing  
caustic steaming  
bleaching  
dyeing  
stiffening  
latex backing<sup>2</sup>  
soil/oil repellent  
finishing

#### Terry toweling

desizing  
caustic steaming

#### Huck toweling

desizing  
caustic steaming

#### 2/2 Twill (Canton flannel)

napping<sup>3</sup>

<sup>1</sup>At Mission Valley Mills, Inc., New Braunfels, Tex.

<sup>2</sup>At Sanford Finishing Corp., Sanford N. C.

<sup>3</sup>At Houston Textile Co., Houston, Tex.



**Terry toweling (cont'd.)**

bleaching  
dyeing  
rewetting/softening finishing

**2/1 Twill (pocket drill)**

sanforizing<sup>4</sup>

**Huck toweling (cont'd.)**

bleaching  
optical whitening

**Shoe duck and sheeting**

no finishing required

Finishing details are contained in 22 pages of process sequence charts which are available in reference 14.

<sup>4</sup>At Brentex Mills, Inc., Brenham, Tex.

These sequences evolved stagewise from initial sequence designs to intermediate to final designs. The initial designs were based on the best available information in the literature and from textile chemical manufacturers. The progression to intermediate and final designs was based on numerous miniplant and semiworks trials on fabrics made in the project but in excess of the 500 yard finished length requirements.

It was possible to produce 500 yard lengths of the 3/2 twill, the Bedford cord, the bark cloth, and terry toweling dyed to union shades acceptable in terms of end to end and side to center levelness, neppy unlevelness, and levelness along discrete yarn lines or segments of yarn.

While physical properties of the finished fabrics were somewhat different from the greige fabrics, the finished fabric properties could be attributed to the process rather than the blend. Expected reduction of tensile strength, abrasion resistance, and tear resistance were no greater than for comparable fabrics from a narrow micronaire range. A detailed presentation of the fabric physical properties has appeared elsewhere (25).

**PREDICTION OF LEVEL DYEING**

Since this project involved blending cotton of widely differing micronaire populations, it was obvious that the GSB testing of these cottons unblended or blended would only indicate that this blend should not be made. What was required was not available, namely, a test which could specify the largest maturity differences in a blend which could nevertheless be successfully dyed in piece form to union shades using cotton dyeing technology representative of the 1970s, that is, dyes and dyeing processes which cover differences. It was felt that even in absence of such a test, dyes and dyeing processes were available which would allow the objects of the project to be attained, that is, the dyeing of 500 yard lengths of the 3/2 twill, the Bedford cord, the bark cloth, and the terry toweling to uniform, level shades of commercial acceptability. Therefore, we proceeded on that basis, but

realized that during the course of the project, materials would be available to attempt the development of such a test.

Experiments were designed to initiate a first-stage development of a test to aid in predicting, in the future, from dyeings on staple samples, the chances of success in level dyeing, with various dye classes, of woven fabrics involving a blend of the micronaire populations investigated in this project. GSB and TRC direct dyeings on staple were not taken to be of use in this frame of reference; the reactive yellow staple dyeings were chosen for this work.

Visual evaluation of all aspects of levelness for the dyeings on the project sheeting fabric was carried out. Reactive and sulfur dyeings were generally commercially acceptable while vat and direct dyeings were generally less than acceptable. It is known, however, that many vat dyes, especially when applied in non-exhaustion processes, cover maturity differences very effectively. The project sheeting was chosen as the woven fabric for this work since it had the least amount of surface profile of any of the project fabrics, and would have been expected to mask any aspects of levelness least of all. It is also to be recalled that the 500 yard lengths of four project fabrics, all reactive dyed, were commercially acceptable in terms of levelness.

It appears that reactive exhaustion dyeings, as done here, on sets of staple samples from high and low maturity populations could be used to predict success in dyeing fabrics from blends therefrom. If K/S values for such yellow reactive dyeings were not in excess of 0.31 level reactive dyeings by non-exhaustion processes could be expected. It is also obvious that dyeing tests based on direct dyeing are too sensitive to maturity differences to be useful in predicting success in the level dyeing of woven fabrics from blends of widely varying maturity.

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## CORRELATION OF WEAR TESTS WITH LABORATORY TESTS OF EXPERIMENTAL AND STANDARD WEAVE COTTON FABRICS RESEARCH PROGRESS REPORT

by

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### INTRODUCTION

Three all-cotton durable press twills, table 1, were selected after consultation with representatives from the Southern Marketing and Nutrition Research Division (SMNRD) laboratories<sup>1</sup>. The objectives were:

1. To determine the performance over wash cycles of dummy leg/cuffs of each fabric.
2. To determine serviceability of slacks of the three twills.
3. To make two-way comparisons between variations in weave or finishes; specifi-

cally twill A compared with twill B, differing in weight, count and weave; next twill B could be compared with C, the same twill differing only in DP finish.

4. To correlate the in-service and laboratory results.

Subjectively and objectively measurable characteristics formed the basis for determining the relative performance. For convenience, data for the twills A, B, and C are generally plotted on the same graphs even though discussed separately.

Table 1. Construction<sup>1</sup> of all cotton durable press fabrics manufactured into work slacks

CODE	WEAVE	COUNT		WEIGHT	FINISH	CURE	
		Warp	Filling				
		Number	Number	Oz./sq.yd.		Min.	
A	3/2 <sup>2</sup>	97	49	7.5	Commercial DMDHEU	330° F.	15
B	3/1	73	40	9.8	Commercial DMDHEU	330° F.	15
C	3/1	75	40	9.8	Experimental Steam set <sup>3</sup>	138° C.	3

<sup>1</sup>All determinations made after slacks were cured at 325° to 330°F., 15 min.

<sup>2</sup>Designed by Cotton Mechanical Laboratory.

<sup>3</sup>Experimental finish developed by Cotton Finishes Laboratory and applied at SMNRD.

### MATERIALS AND METHODS

#### Twills

A finishing plant desized, scoured, mercerized, and dyed the twills brown with sulfur dye. The experimental 3/2 twill was designed by the

Cotton Mechanical Laboratory. For yardages of the standard 3/1 twill and the 3/2 twill, the DP finish was: commercial DMDHEU 25 percent; magnesium chloride catalyst, 5 percent; with acrylic hand builder and cationic softener; cured

<sup>1</sup>Cotton Mechanical and Cotton Finishes Laboratories.



at 330° F. for 15 minutes. Additional yardage the 3/1 twill was padded with: Aerotex 235, 5 percent; Permafresh 183 DMDHEU, 5 percent; mixed catalyst, 1 percent; Seyco lube 45, 2 percent; water; pH of pad bath was 3.5; the fabric was cured, Steam Set, at 138° C. for 3 minutes in SMNRD laboratories.

#### *Slacks*

The twills were manufactured into 36 pairs of slacks, sizes 32/30 and 34/30, of each fabric, and dummy leg/cuffs, size 32/30. Slacks and dummies were cut by a pattern with trim-cut legs without waistline pleats; sewed; pressed on hot head press; and cured for 15 minutes at 325° to 330° F. in a large plant of a jean and casual slacks manufacturer. Impressively careful controls were kept of each step in producing and finishing the slacks. Dimensions of the finished dummy leg/cuffs were approximately: length, including 1-3/8 inch cuff, 12 inches; circumference at bottom of cuff, 15-1/4 inches; at top of leg, 16-3/4 inches. The front half of the dummies was smaller than the back half, of course, like the slacks. Because the Steam Set finish was applied to half-width fabrics, the lay of the garment pieces allowed fewer dummy legs than the full width twills. Subsequently, cured slacks were cut off to provide equal numbers of dummies needed for the statistical design.

#### *Wearers*

Men living in married students' apartments and maintenance/operation personnel of The University of Tennessee wore slacks of each fabric. Two days of wear followed by a wash/tumble dry to 10-to 12-percent moisture content<sup>2</sup> constituted a wear cycle; thus the 5th cycle comprised 10 days' wear and 5 wash/tumble dry. The wash formula and drying procedure are as follows:

#### *Wash formula and drying procedure for slacks and leg cuffs*

Load: 4½ lb. (slacks, dummy cuffs, or white squares mixed)

Wash temperature: 120° ± 5° F. high level water

Detergent: Tide XK — 1½ cups

Time: 10 minutes

Rinse: 105° to 110° F.

Second rinse: 105° to 110° F.

Add 2 tablespoonsful of Velva Soft G stock solution (Sanitizer-Softener)

Extraction: Remove from washer; shake or untangle; zip up zipper if necessary, return cuffs to position

Dry: Tumble dry in electric dryer to 10 to 12 percent moisture.

Remove from dryer: Shake and hang by cuffs on slacks hanger; complete drying with room air circulated by small floor fan. Slacks are hung individually from a large garment rack.

#### *Sampling*

As controls and for comparisons, two dummies and two pair of slacks from each fabric were held, unlaundered. Additional unlaundered items were sampled to obtain specimens for determination of properties for the original fabrics. Two pairs of slacks and two dummy leg/cuffs of each fabric were washed once and tumble dried, rated by judges, and sampled for physical properties. The three judges rated all slacks, individually, as soon as each individual pair reached the 5th, 10th, and 15th wear cycle; thus the average values for the three samplings would represent a different number of garments. Six pairs of slacks of each fabric were withdrawn from service after ratings following the 5th, 10th, and 15th wear cycle; these slacks are to be cut into specimens for physical testing.

Dummy leg/cuffs were rated after every 5th cycle; after each 10th wash/dry cycle (10 through 70), two dummies of each fabric were withdrawn for determination of physical properties.

#### *Procedure*

All specimens were conditioned according to ASTM: D 1776-67<sup>3</sup>. Number of yarns per inch and weight were determined according to ASTM: D 1910-64; fabric stiffness, ASTM D 1388-64 (FRL Cantilever Bending Tester); and tearing strength, ASTM: D 1414-63 (Falling Pendulum apparatus).

Surface appearance, seam appearance, and crease retention, front and back, were evaluated by following AATCC Test Methods 124-1969, 88B-1970, and 88C-1970, respectively<sup>4</sup>. Warp and filling specimens for wrinkle recovery were creased face-face; additional ones were creased back-back; thus recovery angles were recorded separately, AATCC 66-1968. Frosting (front and back creases, seams, edges of cuffs) and visual color change were rated according to the AATCC Gray Scale for Color Change and compared with an unlaundered item. Color Change was obtained with a Photovolt photo-electric reflection meter 670<sup>5</sup>.

Abrasion damage was judged by a modification of the method proposed by Markezich<sup>6</sup>.

<sup>2</sup>Koenig, P. A., and Knoepfler, N. B., A technique for the estimation of moisture of cotton materials during tumble drying. *Amer. Dyestuff Repr.* 57: 41-43. 1968.

<sup>3</sup>American Society for Testing and Materials. Book of Standards Part 24, textile materials — yarns, fabrics and general methods. 1970.

<sup>4</sup>American Association of Textile Chemists and Colorists. Technical Manual. 1970.

<sup>5</sup>Photovolt. Operating instructions for reflection meter 670. 1970.

<sup>6</sup>Markezich, Anthony R. Unpublished. SMNRD, ARS, USDA.



Slacks were examined before and after each wash/tumble dry and defect designation charts were completed as needed for recording accidental damage, stains, tears, or other wear.

## RESULTS AND DISCUSSION

**Color change — Visual.** — Few students were pleased with the brown color. Reasons for dissatisfaction of wearers with color included: (a) dislike the shade of brown; (b) color did not match or blend with shirts and ties; (c) “cannot wear same color slacks to class or work every day because everyone would think you had only one pair.”

Judges rated color change as less in dummy leg/cuffs than in worn slacks, of course. Twill A (the 3/2, 7.5 oz. with commercial finish) had the best color retention as is shown in figure 1.

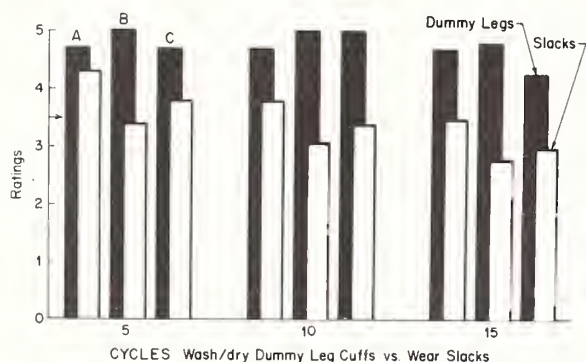


Figure 1. Color change ratings for dummy leg/cuffs after 5, 10, 15 wash/tumble dry cycles compared with slacks in service for 5, 10, 15 wear cycles (one cycle = 2 days/one wash)

### Frostings

This sulfur brown is particularly subject to frosting. Twill A rated acceptable, 3.5, (fig. 2) or better for both creases and seams throughout the 15th wear cycle for slacks or 70 washes for dummies. Frosting was less apparent in dummies. Extremely poor crease retention in *dummies* of B and C (3/1, 9.7 oz. twill with commercial and Steam Set finish, respectively) probably contributed to the acceptable rating; less frosting occurred along creases or where creases had been originally.

Although during manufacture of slacks and dummies the “seam busting,” hot head press and oven conditions were identical, apparently the slacks and dummies cured differently — the dummies were better and more evenly cured. In comparing the slacks with cut-off-slacks through 15 washes, the cut-off-slacks received lower ratings for crease retention. A possible explanation is that slacks were dried to 10- to 12-percent moisture, removed from the dryer and hung by cuffs to continue drying at room

temperature or with air circulated by a small electric fan. Thus the weight of the slightly moist slacks (together with pocketing and waist-band) may have contributed to reestablishment of creases after wash/tumble dry.

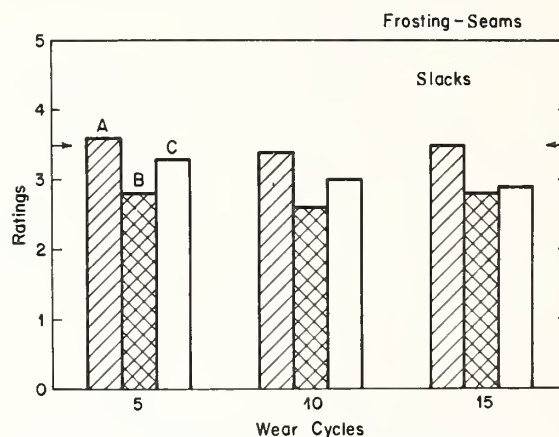


Figure 2. Frosting along seams of slacks after 5, 10, 15 wear cycles (one cycle = 2 days/ 1 wash)

After 20 to 25 repeated launderings, the differences in crease retention between dummies and cut-off-slacks became more noticeable. For example, crease retention in cut-off-slacks of twill B decreased linearly to the 20th wash/tumble dry and then ratings merely fluctuated slightly from 20th through the 50th wash cycle; dummies, on the other hand, regained and improved in crease retention, (fig. 3).

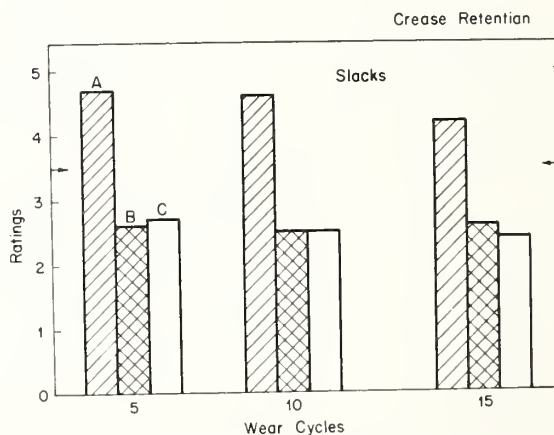


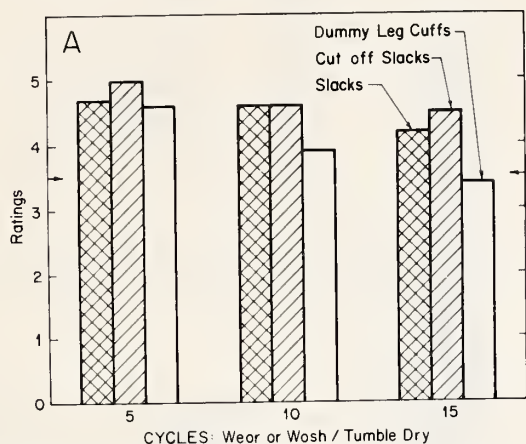
Figure 3. Crease retention in slacks after 5, 10, 15 wear cycles

### Crease retention

Slacks of twill A rated good, 4.2 or above, in crease retention at each judging. But creases in slacks of B and C were poor (fig. 4). Performance of this 3/1 twill with either finish would not readily satisfy consumers.

After one wash/tumble dry cycle without

wear, slacks appeared to have an uneven cure — A rated 4.4; slacks B, 3.2; and slacks C, 3.0. Also within a pair the retention of creases varied from poor, above the ankle, to slightly below average in the area above the knee.



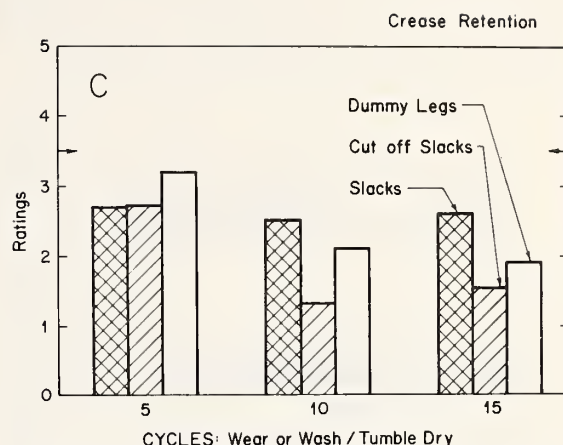
**Figure 4.** Crease retention in slacks of 3/2 twill (7.5 oz, commercial DP finish) after 5, 10, 15 wear cycles compared with cut-off-slacks and dummy leg/cuffs after equivalent numbers of wash/dry cycles

**Cut-off-slack cuffs.** — Because of the marked differences between aesthetic properties of the dummies and the cut-off-slacks of twill C, noticeable even after the first wash, we decided to explore the correlation *OR* differences among dummies, cut-off-slacks and slacks of the three twills. Slacks, size 32/30, were cut off to provide two dummy legs of each fabric for determination of physical properties after each 10 wash/tumble dry cycles (10 through 70) and of aesthetic ratings after each 5 cycles.

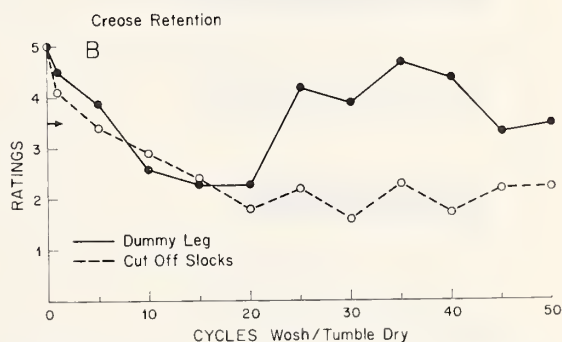
We rather expected the results of the cut-off-slacks to be closely related to data from the slacks. However, the three categories (slacks, cut-off-slacks, dummies) often received different ratings. Figures 5 and 6 illustrate lack of agreement between ratings for the three categories of twills A and C.

#### Appearance

**Seams and fly.** — After the 5th, 10th, and 15th wear cycle, inseams and outseams in slacks of the commercial 3/1 twill, with either finish, rated 3.2 — 3.4. Seams in only A (3/2 twill) rated above 3.5 at all judgments. Likewise the appearance of the fly was 3.4 to 3.7 in the 3/1 twill with commercial and experimental finishes; however, the fly in twill A had the best appearance.



**Figure 5.** Crease retention in slacks of C twill (3/1, 9.7 oz., Steam Set finish) after 5, 10, 15 wear cycles compared with cut-off-slacks and dummy leg/cuffs after equal numbers of wash/tumble dry cycles



**Figure 6.** Crease retention in dummy leg/cuffs compared with cut-off-slacks of B twill (3/1, 9.8 oz. commercial DP finish) after repeated wash/tumble dry cycles

*Average surface smoothness of fabrics in slacks.* — In evaluating surface appearance USASI [United States of America Standards Institute]<sup>7</sup> sets a minimum standard of 3.5 for work trousers. The slacks after one wash/tumble dry without wear rated as follows: A, 4.1; C, 3.9; and B, 3.4. Within a fabric, average ratings for surface appearance were fairly constant from the 5th through the 15th wear cycle. The 3/1 twills had acceptable ratings after wear, 3.9 to 3.6; yet the surface smoothness of A was rated 4.6 to 4.0, slightly above that of the commercial twill.

#### Areas of worn slacks

Of the seven areas rated for surface smooth-

<sup>7</sup>United States of America Standards Institute. USA Standard Performance Requirements for Textile Fabrics. 1968.

ness, four (seat, knee hollow, knee front, lap) of the 3/2 experimental twill slacks showed essentially no difference at the first judging, but ratings after the 15th wear cycle show why "average" surface smoothness is misleading in evaluating performance of garments (fig. 7).

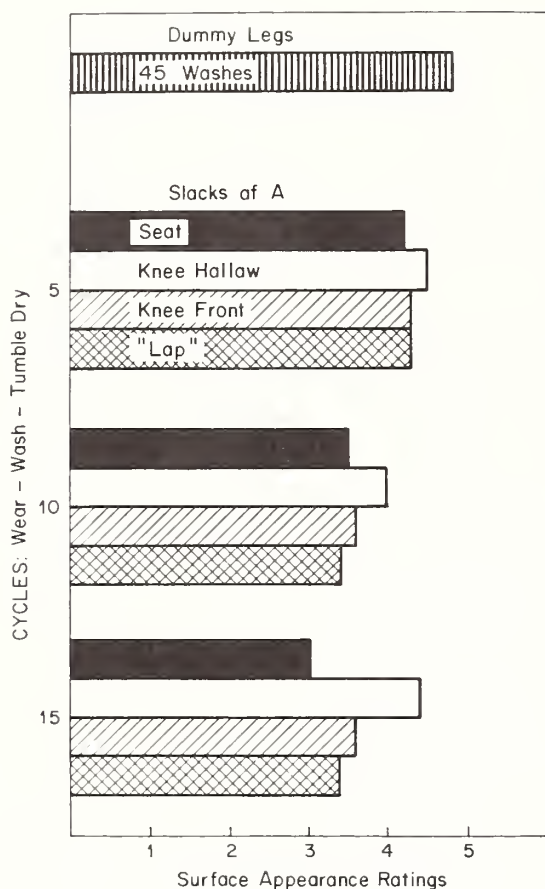


Figure 7. Surface appearance of four areas (seat, knee hollow, knee front, and lap) of twill A after 5, 10, 15 wear cycles compared with dummy leg/cuffs laundered 45 times.

In the slightly tapered leg slacks, the knee area wrinkled or mussed differently for the three fabrics. Because of abrasion damage, the wash/tumble dry cycles for the cut-off-slacks of Twill C terminated at the 45th cycle. In figure 8 the small differences between B and C are probably not significant. Although the ratings of surface appearance in A decreased, the rating after the 15th cycle was slightly above the minimum standard of 3.5. Ratings for B and C indicate this weight (9.8 oz.) twill with either finish would not be acceptable for casual slacks.

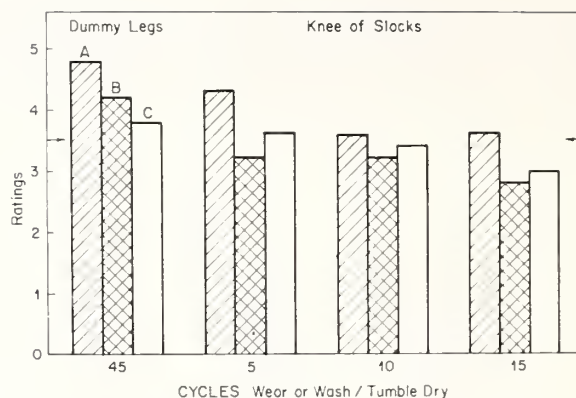


Figure 8. Surface smoothness in fabrics of knee area in slacks after 5, 10, 15 wear cycles compared with dummy leg/cuffs after 45 wash/dry cycles.

### Wrinkle recovery

By using as a minimum standard 125° of wrinkle recovery in each of warp and filling set up by USASI<sup>17</sup>, the crease recovery angle (warp + filling) A, B, C, in dummies was satisfactory to excellent (fig. 9). If the performance of cut-off-slacks is indicative of what we will find in the work slacks, then only twill A will meet minimum requirements for work slacks.

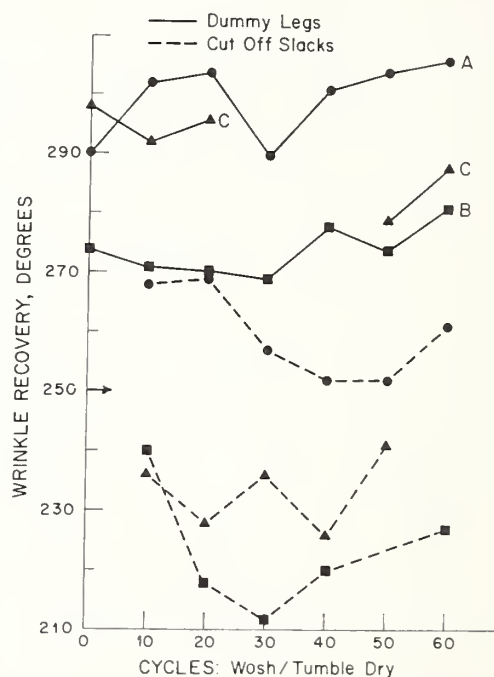


Figure 9. Wrinkle recovery angle (warp plus filling, face-face and back-back) of three all-cotton DP twills in dummy leg/cuffs compared with cut-off-slacks after repeated wash/tumble dry cycles.



Figure 10 compares wrinkle recovery angles, creased face-face of twill B in dummies with that in cut-off-slacks. By using these data, we may predict there probably will be little correlation between slacks and dummies.

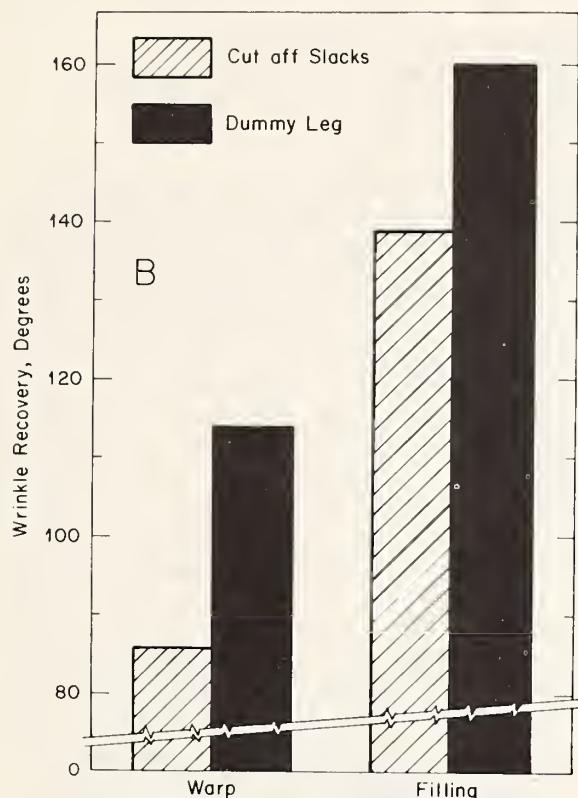


Figure 10. Wrinkle recovery angle (creased face-face) of twill B in dummy leg/cuffs and in cut-off-slacks after 20 wash/tumble dry cycles.

Percent nitrogen (Kjeldahl method) in A, B, C slacks before and after one wash was determined.<sup>8</sup> Another laboratory measured warp and filling wrinkle recovery angles for three areas along the outseam: above ankle, near knee, and adjacent to side pocket. Differences in percent nitrogen and WRA appear to substantiate our earlier hypothesis that the cure was good for the dummies, hung singly in the pass through the oven, but uneven in the slacks hung by the cuffs.

Preliminary investigation of differences in wrinkle recovery between inseam/ankle and outseam/ankle areas added further confirmation that cure was uneven from cuff to waistline and from inseam to outseam. For example, in one pair of slacks the warp WRA of inseam area was 20 degrees less than that of the outseam area (116° vs. 136°).

#### Hand (tactile observation)

The hand of dummies and slacks, as received from manufacturer, was best described by one wearer as "stiff and boardy." One wash/tumble dry cycle improved the hand. Ratings for twills A and C indicated no difference. Judges were not able to detect differences between the 3/1 twill with different finishes, but rated twill A (3/2) as 4.0 to 4.6, definitely superior to the heavier twill with the same commercial finish.

#### Flexural rigidity (stiffness)

After five wash/tumble dry cycles, flexural rigidity of twills A and B with commercial DP finish decreased 76 and 72 percent, respectively (fig. 11). The generally accepted explanation for this rapid decrease in "hand wash down," apparently excess resins are removed from the surface during the mechanical wash/tumble dry cycle. The steam set finish as applied and cured in this project resulted in a twill less stiff; however, other characteristics are probably of greater importance to consumers who may have become accustomed to the original boardiness of durable press items.

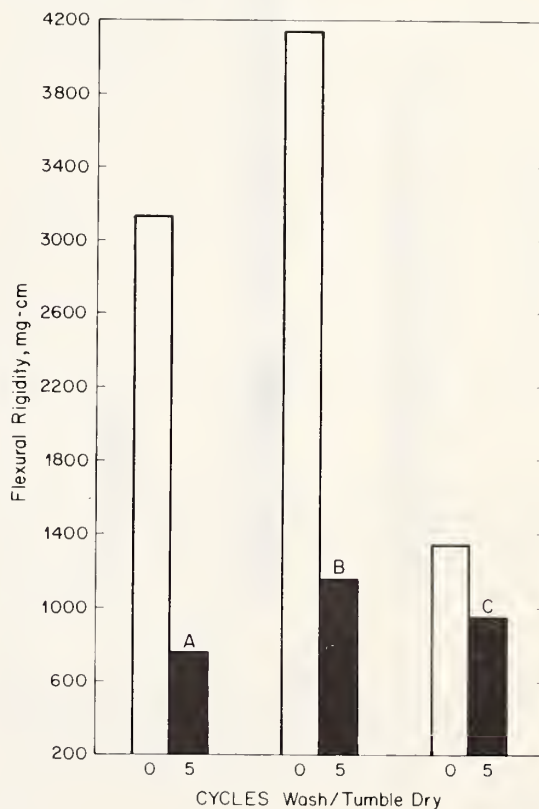


Figure 11. Flexural rigidity of warp (face-Up) of three all-cotton DP twills in dummy leg/cuffs before and after 5 wash/tumble dry cycles.

<sup>8</sup>Chemical Finishes Laboratory and Textile Testing Group, SMNRD.

Stiffness of cut-off-slacks after 10 wash/dry cycles was less than that of dummies (fig. 12), attributable to the difference in cure of slacks and dummies of the same fabric. Flexural rigidity of cut-off-slacks and dummies was still decreasing at the 60th wash interval. The decrease was not at the same rate between evaluations and not at the same rate for all fabrics (fig. 13); however the decrease was essentially a linear relationship. In general, for the dummies flexural rigidity, which takes into account fabric weight, was greater at any interval than that for the cut-off-slacks. Thus the difference was a further indication of either an over-cure of the dummies or an under-cure of the slacks. It may indicate that to obtain a good cure through the top (heavier part of the slacks with waistband and pocketing) the lower legs will be over-cured.

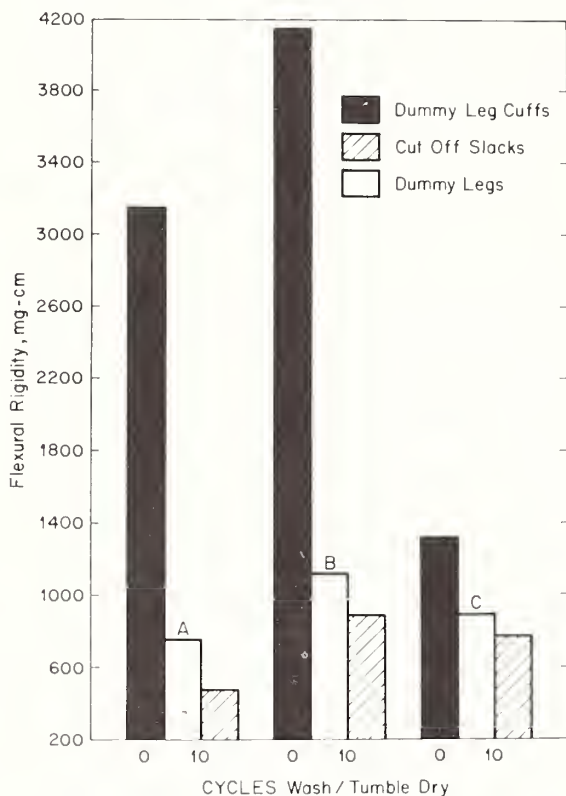


Figure 12. Flexural rigidity of warp of three all-cotton DP twills in dummy leg/cuffs and cut-off-slacks before and after 10 wash/tumble dry cycles.

#### Cleanings

Ratings for degree of cleaning of twills in slacks after the three wear intervals were good to

excellent; the rating for twill B is probably not significantly higher than that for C. The excellent ratings for A, 4.9 to 5.0 indicate consumers would be well pleased with the appearance after refurbishing of these experimental twill slacks.

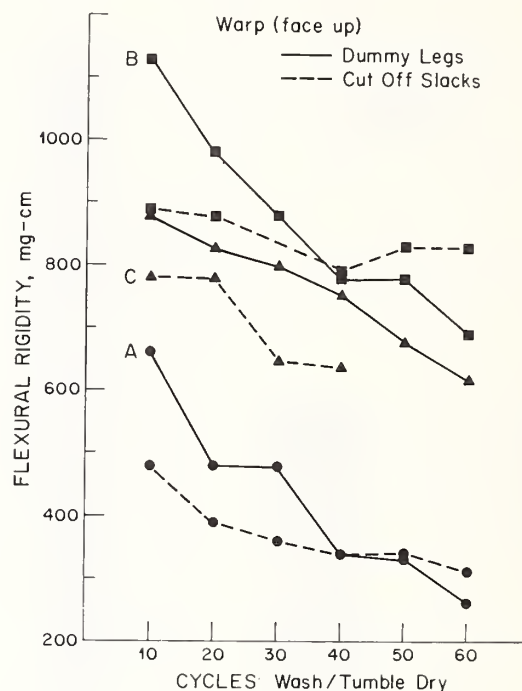


Figure 13. Flexural rigidity of three twills in dummy leg/cuffs compared with cut-off-slacks, 10 through 60 wash/tumble dry cycles.

Trite yet true: it is a long way from the laboratory to fullstream production in a plant; and laboratory and field service tests do not correlate. Perhaps one contribution to the lack of correlation has been the differential cure in dummy leg/cuffs taken to represent real garments worn by people.

#### ACKNOWLEDGMENTS

The author wishes to express appreciation to: The University of Tennessee administrators for permission to recruit wearers; students and maintenance/operation personnel who wore the slacks; Mike Donoghue of the Textiles and Clothing Laboratory and to undergraduate and graduate students who worked as laboratory aides and judges; manufacturer of the slacks; and the finishing plant who donated the standard twills and the commercial finishes.



## STRENGTH LOSSES AND STRUCTURAL CHANGES IN COTTON PRINT CLOTH CROSSLINKED WITH DIMETHYLOLETHYLENE UREA

by

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(Presented by Leon Segal)

The application of durable-press finishes to cotton fabric is accompanied by losses in tensile strength, tearing strength, and other properties. These losses have been attributed to factors induced mainly by the crosslinking of the cellulose molecules, a conclusion derived from analyses of the results from textile or physical testing of treated fabrics. A subject that has received little consideration in these studies is the proportion of the losses that originates from changes in the chain length of the cellulose molecule, changes brought about by the chemical reactions with the crosslinking agents that produce the desired crease-resistant finish. Information on contributing to this subject first appeared when reports were made of the effect of formaldehyde crosslinking of cotton on the chain length of the cellulose molecule. In these studies relationships were found between chain length and textile properties.

In the present study dimethylolethylene urea (DMEU) and a zinc nitrate catalyst were applied to 80 x 80 cotton print cloth in a commercial manner but with varying times of cure. The objective was to define the causes of the strength losses resulting from the durable-press treatment. Cure times ranged from 1/4 minute to 12 minutes. Reagent concentrations were 0.03 M for the zinc catalyst and 0.55 M for DMEU and for ethylene urea (EU). Ethylene urea, the parent compound of DMEU that is incapable of crosslinking with the cellulose molecule, was used with catalyst to approximate the effect of acid catalyst on the cellulose molecule in the presence of the proton-accepting ethylene urea moiety. In addition to treatment with DMEU — catalyst, fabric was also treated with EU + catalyst as just mentioned, with catalyst only, and with water only. Fabric samples were padded through two dips and two nips, then placed on pin frames at original dimensions for drying at 70° C. for 5 minutes followed by curing at 160°. Fabrics were subjected to physical testing, and parts were nitrated to provide soluble samples for study by viscometry and by gel permeation chromatography.

The amount of DMEU reacted with the fabric, as indicated by the nitrogen content, displayed a small, steady increase with cure time. Durable-press rating became constant after the 1/4-minute cure. Wrinkle-recovery angles (W+F), conditioned and wet, increased and leveled off after the 3-minute cure. Significant, large decreases in breaking strength, tearing strength, and abrasion resistance occurred which confirms previous findings. Moisture regain behaved similarly with cure time.

Comparison of the above results with those from fabric treated with EU + catalyst, with catalyst alone, and with water alone showed that the breaking and tearing strengths for the fabric treated with DMEU + catalyst dropped precipitously with cure time, but leveled off after the 2-minute cure. For the sample treated with water only, breaking strength decreased slightly in a linear manner. Tearing strength, however, decreased more significantly following a smooth curve. The large losses in breaking and tearing strengths for the fabric treated with catalyst only also followed smooth curves. The same is true of the fabric treated with EU + catalyst, except that the losses were much less than the losses for the fabric treated with DMEU + catalyst.

The changes in degree of polymerization (DP) with cure time for the fabric treated with catalyst only produced the smooth exponential curve normally observed in the acid hydrolysis of cellulose. The fabric treated with EU + catalyst gave a similar curve but with less extensive degradation of the molecule. The curve for the fabric treated with DMEU + catalyst was found to lie between those of fabrics treated with EU + catalyst and with water only. The position of this curve with respect to those of the other treated fabrics suggests that in this fabric there are molecular interchain linkages which were not removed during the nitration process for preparing a soluble derivative — this is in effect, then, chain extension.

The relationships between breaking or tearing strengths and DP for the fabric treated with



DMEU + catalyst are markedly different from those of the other samples. The data for the latter samples all lie on a smooth curve covering a wide range. The data for the fabric treated with DMEU + catalyst depart abruptly in a single large drop from that of the untreated fabric, and clump together in a curve of very limited range. The difference in response of the fabric to DMEU and to EU is very marked. The relationship between total losses in breaking strength for the treated fabrics and their moisture regains is linear for all the fabrics. The data for the fabrics treated with EU + catalyst and catalyst only fall on parallel lines with rather small difference in moisture regain values between them. This indicates that the accessible structures of the fibers in these fabrics are very similar. In the case of the fabric treated with DMEU + catalyst, however, moisture regain is much reduced, showing a marked progressive reduction over a small range of strength loss. An inaccessible structure, becoming more so with cure time, would give rise to this.

The total strength loss of crease-resistant fabric produced by treatment with DMEU + catalyst can be separated with the help of data from fabric treated with EU + catalyst into two components, one component arising from crosslink embrittlement and one arising from molecu-

lar chain cleavage (degradation) of the cellulose. When the breaking strength data are reduced to percentages and plotted against the reciprocal of DP, linear relationships are obtained that show the proportion of strength loss arising from each source with respect to DP. In the early cure times the predominant strength loss comes from crosslink embrittlement, but this proportion drops rapidly. At the 3-minute cure time, which corresponds to the extent of cure normally used in durable-press treatments, 73 percent of the total strength loss arises from crosslink embrittlement; this drops to 58 percent on lengthening cure time by 1 minute. Molecular degradation accounts for 27 percent, then 42 percent of the loss, respectively. In over-curing of the fabric, molecular degradation becomes the major source of strength loss. With an 8-minute cure, molecular degradation is responsible for 52 percent of the total strength loss. This proportion increases as over-cure increases. Substituting the reciprocal of time of cure for that of DP shows that the proportions of loss assignable to crosslink embrittlement and to degradation begin to change at a fast rate after 1/2 minute of cure. The proportions become equal between 6-1/2 and 7 minutes of cure, after which strength loss from degradation becomes the major component. The data for tearing strength indicate similar trends.

## FORMATION OF INCLUSION COMPLEXES BY LIQUID AMMONIA TREATMENTS OF PREVIOUSLY CROSSLINKED COTTONS

by

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(Presented by R. H. Wade)

The changes in physical properties of yarns and fabrics, during application of chemical swelling treatments to previously crosslinked cotton, were investigated. The conversion of the crystalline lattice from cellulose I to cellulose III is known to occur in kiered cotton yarn treated with liquid ammonia followed by slow evaporation of the ammonia from the cotton. It has now been shown that the cellulose I crystalline lattice of cotton yarn previously crosslinked with DMEU is converted to cellulose III by treatment with liquid ammonia followed by slow evaporation of the ammonia. This remarkable penetration into the crystalline lattice structure of a previously crosslinked cotton also occurs when certain organic amines are used as the swelling agent. The ethylenediamine complex of crosslinked cellulose was formed by

direct application of the diamine at room temperature to DMEU-treated yarn.

Recent work in these laboratories has shown that stable inclusion complexes of chloroform in cotton are readily formed by treatment of yarn with chloroform dissolved in liquid ammonia followed by evaporation of the ammonia. As much as 15 to 20 percent chloroform can be trapped in the yarn. When this occurs, the crystalline cellulose I lattice is replaced with an amorphous or noncrystalline cellulose as determined by X-ray diffraction. It has now been found that when previously crosslinked cotton yarn is treated with 50 percent chloroform in liquid ammonia (vol./vol.) evaporation of the ammonia leaves as much as 11 percent chloroform trapped in the cotton, and the cellulose I lattice is replaced by an amorphous cellulose

X-ray pattern.

Physical data were obtained on some of the products treated with ammonia and chloroform. Treatment with liquid ammonia alone greatly improved the strength and elongation of DMEU crosslinked cotton yarns, when this was done in the slack state. The strength of previously crosslinked yarn was increased 51 percent while elongation was increased twofold. The energy-to-rupture, after ammonia treatment, was increased fourfold to approximately the same value as the kiered yarn not crosslinked at all. Inclusion of trimethylolmelamine as a crosslinking agent in kiered cotton yarn by application from liquid ammonia solution and subsequent curing to effect crosslinking, produced a crosslinked cotton which had the strength reduced only by 12 percent, the elongation-at-break increased by 68 percent, and the energy-to-rupture unchanged, as compared to the original kiered yarn. The similarity of the physical properties obtained for the treatments under slack conditions, using liquid ammonia on previously crosslinked (DMEU) yarns and on subsequently crosslinked (TMM) yarns, is interpreted as being due to the effect of swelling by ammonia rather than the effect of crosslinking of cellulose chains.

Application of chloroform in liquid ammonia to crosslinked and kiered cotton fabric held under tension was carried out in a continuous process. It was demonstrated that conditions which maintain the original dimensions of the fabric greatly limit the extent of cellulose swelling, and the amount of chloroform bound in the fibers. In a typical run, 3-percent chloroform was included in fabric.

A series of treatments were also applied to cotton fabric in the slack condition. In kiered fabric, 19 percent chloroform was trapped in the fibers, while in crosslinked fabric, 11 percent chloroform was similarly bound. Shrinkage of 14 percent in the warp and 7 percent in the fill was obtained on crosslinked fabric by treatment slack with liquid ammonia. Shrinkage of 9 percent in the warp and 5 percent in the fill was obtained on crosslinked fabric by treatment slack with 50 percent chloroform in liquid ammonia.

Dyeing from liquid ammonia was shown to be more effective on kiered cotton fabric than on crosslinked cotton. It thus appears that a variety of practical effects may be realized from the formation of inclusion complexes of dyes or finishing agents in cotton and that these applications are effective before or after crosslinking.

## ACCESSIBILITY TO AQUEOUS MEDIA OF DURABLE-PRESS COTTON FABRICS

by

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(Presented by Mary L. Nelson)

The satisfactory performance of cotton textiles by the consumer is intimately related to the interaction of fabrics with water and water vapor. Perspiration and humid climates raise the moisture content of garments during wear and in storage. Removal of soil by washing (or even in "spotting" before drycleaning) involves the wetting-out of the fabric. Good performance depends on the ability of the fabric to recover its initial appearance after deformation under various moisture conditions during wear or washing and drying.

The relationships between the currently used criteria of good performance — wrinkle recovery angle and appearance rating — and a variety of parameters of the accessibility of cotton to aqueous media were examined in detail. Fabric was treated with a commonly used crosslinking reagent (dimethyloldihydroxyethyleneurea, DMDHEU) by three different processes (pad-

-dry-cure, mild cure, and steam cure) at several levels of add-on (2 to 20 percent) to produce fabrics with a wide range of properties associated with good performance. For further comparison, formaldehyde was applied by the Form D and Form W processes, known to give divergent wet and dry properties, and by a recent modification of the vapor-phase process. The usual strength and recovery measurements were obtained on these modified fabrics. Swellability was measured by water retention, alkali centrifuge value, and yarn-untwisting data. Accessibility to iodine sorption and to deuterium exchange were measured but gave inconclusive results. Moisture sorption, measured at selected relative humidities between 11 and 93 percent gave an indication of accessibility under minimum to moderate swelling conditions. Internal surface areas were also calculated.

Wide ranges in wrinkle recovery angle (180°



to 290°, warp plus filling) and appearance rating (1.0 to 3.7) were achieved, with the usual concurrent losses in breaking and tearing strengths and abrasion resistance.

Water retention was found to be inversely correlated with conditioned wrinkle recovery angle and with tumble-dried appearance ratings, although the DMDHEU fabrics and the formaldehyde-treated samples lay on separate curves. Water retention values of the DMDHEU fabrics and the vapor-phase formaldehyde samples showed good negative correlation with line-dried ratings and wet-wrinkle-recovery angles, but the Form D and Form W samples had much better recoveries than predicted by the correlation for the other samples. Alkali centrifuge values were roughly inversely related to tumble-dried ratings and conditioned recovery angles; for line-dried ratings and wet recovery angles, good inverse correlations with ACV were found, but each process gave a separate relationship. Yarn-untwisting values exhibited a good inverse correlation with both line-dried ratings and wet recovery angles for all processes; but with tumble-dried ratings and conditioned recovery angles, only the DMDHEU fabrics exhibited close negative correlation, while the three formaldehyde sets were different. The Form W samples had very low yarn-untwisting values and low tumble-dried ratings, whereas the vapor-phase process yielded samples with intermediate yarn-untwisting values and high ratings. The Form D samples had intermediate values of both parameters.

Moisture sorption data at low relative humidities showed some interesting differences among treatments. Pad-dry-cure and mild cure processes produced fabrics with regains below that of the control but regains of steam cure fabrics were higher than that of the control. These differences between treatments decreased at higher relative humidities until at 93 percent R.H. all three series of DMDHEU fabrics were much reduced below the control. Among the formaldehyde treatments, at 11 percent R.H. the regains of vapor-phase and control fabrics were about equal, whereas those for Form D and Form W fabrics were higher. As the relative humidity increased, the regain of the vapor-phase samples became progressively lower than that of the control, while that of the Form D and Form W fabrics became progressively greater. Correlation of regain at 65 percent R.H. with wet and with conditioned WRA, or with line-dried appearance ratings, gave separate lines for each of the DMDHEU series, whereas regain versus tumble-dried ratings tended towards a single curve for all three processes.

Let us consider some possible implications of these data. Resilience, as measured by wrinkle

recovery angle and appearance ratings, is obviously related to the amount of crosslinking agent introduced by a specific process and is also affected by the nature of the process. Two aspects of the crosslinking reaction are important — the chemical and the physical. Such chemical factors as the length of the crosslinks and the presence of uncrosslinked material (trapped resin, substituent groups, and intramolecular bridges) undoubtedly influence resilience. These have been discussed by others; no additional data are presented here. Probably of equal importance is the physical location of the crosslinks; that is, their placement in relation to fiber structure. The cotton fiber is a hollow, collapsed tube whose wall is composed of several layers. Each layer consists of fibrils which are large bundles of microfibrils; these latter are aggregates of elementary fibrils. Channels and pores separate some of these structures; their volume, size, shape, and distribution can only be deduced from indirect measurements. It is reasonable to presume that crosslinks can be located in any or all of the following positions: between major structural units (the layers of cellulose in the cell wall); between microfibrils and elementary fibrils within these layers; and between molecules on the surface of the same elementary fibril. The proportions of crosslinks in these various locations should have considerable effect on the mechanical properties of the fiber, and hence on the behavior of the fabric.

When crosslinking agents are applied as aqueous solutions, the water swells the fiber so that the reagent can penetrate into all but the most highly ordered regions. If reaction takes place while the fiber is water-swollen (as in the Form W process), the distance between major fiber elements is probably so great that the possibility of crosslinks bridging the channels which separate the major elements is small. Drying before heat-curing shrinks the fiber walls so that crosslinks can form not only between microfibrils and elementary fibrils (as in wet-reacted fibers) but also between the walls of the now collapsed pores and channels. Fibers reacted in the moist state (steam-cure and vapor-phase processes) or partly swollen (Form D process) would tend to be intermediate in number of crosslinks between major elements.

With this in mind, consider the present data on swellability in aqueous media in relation to recovery properties. Water retention measures the extent to which the original water-holding capacity of the fiber is still available after the crosslinking reaction. Water retention correlates reasonably well with the total internal void volume determined by other methods. This internal volume is believed to exist as pores and



channels in the fiber. It can be inferred that, in fabrics with low water retention, at least some of the crosslinks must be located between major fiber elements (across the sites of channels and pores that existed in the water-swollen fiber). Apparently, crosslinks in these positions are necessary for good tumble-dried appearance and conditioned wrinkle recovery. Moisture sorption at low relative humidities, which indicates the internal surface area, substantiates this; fabrics with the highest regains have the poorest tumble-dried ratings.

Yarn untwisting values are sensitive indicators of the extent of fiber swelling in water. Even a low level of reaction greatly decreases the amount of untwisting. Crosslinks that prevent fiber swelling must be important for good line-dried appearance and wet recovery, since there is a high negative correlation between yarn-untwisting values and good appearance ratings and recovery values. Most of the crosslinks affecting yarn-untwisting are inferred to be between microfibrils and elementary fibrils, or along their surfaces, rather than between major fiber elements, since the Form W fabrics with the highest water retention values (presumed to indicate few inter-layer bridges) have very low yarn-untwisting values.

The alkali centrifuge value, which results

from chemical swelling, indicates the extent to which crosslinks restrain the swelling of the highly ordered regions. One infers that the most effective location of such crosslinks is between the layers of the fiber wall, although those between fibrils and microfibrils will also exert an effect. This inference is based on the similarity of water retention and alkali centrifuge values and on the knowledge that gross physical restraint (yarn twist, fabric structure) will restrict swelling in alkali. For good tumble-dried appearance and conditioned wrinkle recovery, sufficient crosslinks must be present to almost completely inhibit chemical swelling, since these properties decline rapidly as the ACV increases. For good line-dried appearance and wet recovery, such is not the case, since other factors are operating.

To summarize: For good wet recovery properties, crosslinks located along the surfaces of elementary fibrils and between them appear to be sufficient; these do not restrict retention of water or swelling in alkali. For good conditioned recovery properties, crosslinks between major structural elements are needed in addition to those at the elementary fibrillar level; water retention, swelling in alkali, and moisture sorption are reduced by the presence of crosslinks at such locations.

## A CATALYST SYSTEM FOR CREASING FULLY CURED DURABLE PRESS GOODS

by

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(Presented by Robert M. Reinhardt)

Numerous chemical finishing processes have been described for producing durable press items that have both creases and smooth areas (9). Although some were never utilized past the laboratory or pilot-plant stage, many of these processes have been tried on a commercial scale and several are in use today. However, in the great majority of these processes, to have both creases and smooth areas, it is necessary to insert the creases before development of a full cure of the chemical finish. The term "full cure" is used here in the sense that fabrics with a full cure have a level of durable press smoothness sufficiently high that the fabric can be utilized, albeit without creases, without the need for further processing of any kind.

Established processes for producing durable press items that contain creases fall mainly into two categories, those that use precure and

postcure techniques (4). Among postcure techniques are the well-known Warnock and Hubner deferred cure process (13), Mizell's garment treatment process (7), Cotton Institute/American Laundering Machinery Institute's formaldehyde/SO<sub>2</sub> vapor phase treatment (11), and Walsh's radiation cure process (12). Precure processes generally employ a high temperature, high pressure pressing to produce a crease in fully cured fabrics, usually of high content of thermoplastic fiber (8). A method which is somewhat between these two clear-cut cases is that of Buck and Getchell in which fully cured fabric is creased by localized application of a catalyst and pressing (1).

Earlier studies on creasing fully cured fabrics have been conducted at this Laboratory. Franklin and coworkers (2,3) used polycarboxylic acids as catalysts and coreactants in crosslinking

cotton for this purpose. Hobart and Mack (5) reported the conditions necessary to break and reform crosslinks through the action of in situ catalyst groups in fabric that has been chemically modified to bear diethylaminoethyl substituents. Kullman, Cashen, and Reinhardt (6) showed that ammonium chloride/phosphoric acid could serve as a low temperature catalyst system capable of creasing and postcuring wrinkle resistant fabric at the unusually low temperature of 100° C.

In recent research conducted at this Laboratory on the catalysis of various finishing treatments for producing durable press fabrics, the versatility of aluminum chlorhydroxide in various catalyst systems has been established (10). Because of the broad applicability of this catalyst, its use was investigated for creasing fully cured durable press goods. This presentation is a progress report of the findings.

Aluminum chlorhydroxide,  $\text{Al}_2(\text{OH})_5\text{Cl}$ , which is often called aluminum hydroxychloride and the 5/6 basic aluminum chloride complex, can function in several catalytic roles depending upon the finishing system used. That is, aluminum chlorhydroxide can provide excellent catalysis by itself in many conventional finishing treatments; it acts as a buffer with strong mineral acids to moderate their catalytic activity; and it gives synergistic effects with many weak acids and salts in which the mixture is a stronger catalyst than either component alone. Furthermore, there is little or no change in the strength and durable press performance properties after storage without an afterwash, even in cotton fabrics finished with combinations of aluminum chlorhydroxide and mineral acids as catalysts. Postcure finishing with aluminum chlorhydroxide catalysis also has been very promising.

In the present work, all-cotton and cotton/polyester fabrics of several fiber blend compositions have been used. Because the creasing of fully cured durable press goods has potential applications in commercial plant processing and in home sewing, both lightweight and heavier weight fabrics were considered. For the same reason, various types of creasing equipment and procedures were investigated. These included the use of commercial-type steam-presses and hot-head presses and curing ovens, and household-type steam-irons and hand-irons. In most of the experiments dimethylol dihydroxyethyleneurea (DMDHEU) was the finishing agent used although dimethylol methyl carbamate (DMMC) also was used. Catalyst systems investigated included aluminum chlorhydroxide alone and activated mixtures containing aluminum chlorhydroxide and certain mineral acids, organic

acids, and inorganic salts. The effects of these and various other parameters upon the success of producing a durable crease have been determined.

Four principal types of creasing were studied: creasing on a commercial steam press followed by oven treatment; creasing on a commercial steam press followed by treatment on a hot-head press; creasing with a household-type hand-iron. The first two techniques are applicable for commercial processing while the last two are suitable for use in the home.

All-cotton fabric requires a more stringent creasing treatment than cotton/polyester fabric to yield a sharp, durable crease. A more active catalyst or higher creasing temperature or both are required as the mechanism involved in all-cotton fabrics seems to be the breaking and reforming of crosslinks in the finished cellulose fibers. The polyester fibers in blend fabrics are not crosslinked by the finishing treatment and, in addition, are thermoplastic. This thermoplastic shaping assists the creasing and makes milder catalysts and treatment conditions operable. The contribution of the thermoplastic fibers can be demonstrated readily by creasing unfinished fabric or finished fabric that has been thoroughly washed to remove the catalyst.

Fully cured goods that had been finished with aluminum chlorhydroxide catalysis (2 percent  $\text{Al}_2(\text{OH})_5\text{Cl}$ ) gave higher quality creases than similar goods finished with zinc nitrate catalysis. If the fully cured fabrics were washed and the catalyst reapplied, markedly poorer creases were produced than when the goods were creased with residual catalyst from the prior finishing treatment present. Apparently once removed, it is not possible for the catalyst to be properly redistributed in the crosslinked cellulose structure.

Other processing parameters that influence the quality of the resulting creases were identified. For example, in finishing the fabric for subsequent creasing, it is desirable to use treatment conditions adequate to give a satisfactory level of durable press smoothness but not to over-cure. Excessively high curing temperatures (160° C.) diminish the quality of the creases that later can be produced in the goods.

Observations have been made on the temperatures necessary for creasing with a hand iron or hot-head press and those for oven treatment after steam pressing. Although the fully cured fabrics were being creased, inordinately high temperatures were not needed. That is, creasing and oven curing at about 140° to 160° were effective in most instances.

The results of this study suggest that fully cured durable press goods can be creased by



techniques that are applicable in commercial plants and in the home. Findings on the interacting effects of many variables including the nature of the finishing agent, the catalyst system, the fabric structure and composition, the finishing treatment, and the creasing technique should be helpful to the industry in achieving this objective.

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SESSION IV: Robert F. Johnson, Texas Tech University, Lubbock, Tex., Chairman

#### ELEMENTAL ANALYSIS OF FLAME-RETARDANT COTTON FABRICS

by

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(Presented by Biagio Piccolo)

Some 15 or more elemental species may be used in flame-retardant compositions applied to cotton textiles. Since performance is closely

related to the concentration level of the added species, rapid and reliable analyses are a necessary part of flame-retardant research and quality



control. With the exception of nitrogen, the direct determination of other elemental species of interest by instrumental methods of analysis is feasible. This presentation considers the application of these methods in the flame-retardant program of the Southern Marketing and Nutrition Research Division.

The method of choice is *x-ray fluorescence*, which has adequate sensitivity for most species encountered in flame-retardant applications, an exception being the nondurable boron compositions. The initial cost of x-ray fluorescence equipment is relatively high (\$25,000.00 or more), but its broad scope and rapidity permit a quick recovery of this investment. Fifty to seventy-five duplicate elemental determinations per 8-hour period can be achieved without difficulty by a single analyst. A typical fee for single determinations of this type by a commercial laboratory is \$7.00. Thus, x-ray fluorescence can permit considerable savings over alternative routes for obtaining equivalent analytical information. In our experience the method is quite reliable for elements heavier than magnesium, except for absorption effects arising in specimens containing large amounts of a heavy element in admixture with a light element sought, or where there are wavelength interferences between elements of interest. Absorption effects can be handled by using appropriate synthetic mixtures of the elements sought as calibration standards. Wavelength interferences can be minimized by pulse height selection techniques when the interfering elements are not too close in atomic number, but employment of a diffracting crystal which can suppress the unwanted radiation is a simpler and equally effective approach. In the case of the serious interference between

the second-order calcium K-beta radiation and the phosphorus K-alpha radiation in specimens which have been laundered in hard water, the use of a quartz analyzing crystal (2d, 6.68 Å.) effectively suppresses the Ca wavelength. The ability of x-ray fluorescence to provide a rapid qualitative analysis of specimens of interest is unmatched by any other technique, and the lack of homogeneity of application of the finish to the fabric can easily be demonstrated.

*Atomic absorption spectrometry* has proved to be a most useful adjunct to x-ray spectrometry in important areas of the flame-retardant program of the Division. It is applicable, in general, to all elements except the nonmetals, with part per million sensitivity. The investment in equipment is about \$5,000 to \$10,000. Sample preparation time for most specimens is lengthy, since the element is ordinarily introduced into the flame as an atomized solution. Flame-retardant fabrics which have picked up magnesium and calcium as a result of laundering conditions are amenable to analysis by simple extraction with dilute mineral acid. Under favorable conditions, boron, which ordinarily is accessible only to spectrographic emission analysis, can be estimated by atomic absorption techniques. An improvement in sample preparation and handling may be expected with the application of graphite furnace atomization, where the specimen can be heated to 2,500° C. and the absorption of the element of interest measured.

These techniques, in conjunction with emission methods where indicated, provide a solid foundation for flame-retardant analysis. Future applications would appear to include both neutron activation and photo-electron analysis, but both await less costly instrumentation.

## INFLUENCE OF ATMOSPHERE AND ADDITIVES ON THE RATE OF FREE RADICAL AND CHAR FORMATION DURING THE THERMOLYSIS OF COTTON

by

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(Presented by Oscar Hinojosa)

When purified cotton is heated, a singlet ESR spectrum is generated, which has a g-value close to that of free spin and does not exhibit any hyperfine splitting. The trapping and stabilization of the free radicals in the heated cotton are probably caused by the formation of ring structures, particularly condensed carbon rings with large resonance energy, during the thermolysis of cotton. The concentration of free

radicals in cotton increases rapidly with increase in temperature and time of heating. The line-width and shape of the ESR spectra for cottons heated over a temperature range from 250° to 350° C. are essentially the same. Consequently, the concentrations of free radicals in heated cotton can be estimated by measuring the peak-to-peak values of the ESR spectra.

Changes in the rate of decomposition of

heated cotton are related to changes in the rate of formation of free radicals during heating. The rate of formation of free radicals in heated cotton is dependent on: temperature of heating; atmosphere during heating; removal of volatile decomposition products during heating; temperature conditioning before heating at different temperature; and the presence of additives which may be introduced, for example, when cotton is modified to impart durable-press or flame-retardant properties.

The influence of atmosphere on the formation of free radicals in cotton was investigated by heating cotton in the ESR sample tube, normally positioned in the resonant cavity of the spectrometer, in such a way that a stream of gas could be flowed through the cotton. The flow of gas through and the rate of heating of cotton were adjusted, so that the temperature of the heated cotton was constant at different rates of gas flow. The effects of time of heating

purified cotton in nitrogen (both static and flowing) and air (flowing only) at 250°, 270°, and 290° C. on the concentration of free radicals formed are shown in table 1. In the case of nitrogen, if the volatile decomposition products were, at least, partly removed by the flowing gas, the concentrations of free radicals formed were greatly reduced. In the case of flowing air, the concentration of free radicals formed was greater than in the case of flowing nitrogen. At 270° and 290° C. the concentration of free radicals formed in cotton in nitrogen (static) and air (flowing) were about the same. After an induction period of about 6 minutes at 290° C., the decomposition products formed in nitrogen (static) apparently accelerated the decomposition of cotton. The higher concentration of free radicals formed in cotton at 290° C. in air (flowing) than in nitrogen (flowing) was probably due to air oxidation.

Table 1: — Effect of temperature of heating and atmosphere on the formation of free radicals in purified cotton

Concentration of free radicals, arbitrary units, at temperature of heating of:									
Time of Heating,	250° C.			270° C.			290° C.		
	Atmosphere								
Min.	N flow	N static	air flow	N flow	N static	air flow	N flow	N static	air flow
1	0.5	0.3	0.4	0.4	0.3	0.4	0.4	0.5	0.5
2	0.4	0.3	0.4	0.4	0.4	0.8	0.6	1.3	1.6
3	0.4	0.4	0.5	0.6	0.7	1.1	0.8	2.0	2.9
4	0.4	0.4	0.6	0.7	0.9	1.4	1.0	3.1	3.9
5	0.4	0.4	0.6	0.7	1.1	1.7	1.2	4.3	4.9
6	0.4	0.4	0.8	0.8	1.2	2.0	1.4	5.9	5.7
7	0.4	0.4	0.9	1.0	1.4	2.3	1.7	7.4	6.7
8	0.4	0.5	1.0	1.0	1.5	2.7	1.9	9.2	7.6
9	0.5	0.4	1.1	1.1	1.9	2.9	2.1	11.0	8.9
10	0.5	0.5	1.2	1.3	2.0	3.1	2.3	13.0	10.0
11	0.5	0.6	1.3	1.3	2.1	3.3	2.5	15.2	11.3
12	0.6	0.6	1.4	1.4	2.4	3.5	2.7	17.6	12.9
13	0.7	0.6	1.5	1.5	2.7	3.7	2.9	20.0	14.6
14	0.6	0.7	1.6	1.5	2.9	3.8	3.1	22.5	16.4
15	0.6	0.7	1.6	1.7	3.2	4.0	3.4	25.0	18.4
16	0.6	0.7	1.7	1.7	3.5	4.2	3.7	27.5	20.6
17	0.6	0.8	1.8	1.8	3.8	4.4	3.9	30.0	23.0
18	0.6	0.8	1.8	1.9	4.0	4.6	4.1	32.5	25.5
19	0.7	0.8	1.9	2.0	4.4	4.7	4.3	35.0	28.0
20	0.7	0.8	-----	2.0	4.7	4.8	4.5	37.5	30.8

The effects of residual decomposition products on the formation of free radicals in heated cotton are also shown in table 2. Samples of cotton were preheated at 265° C. in nitrogen (static) (A) and vacuum (B) for 10 minutes; then they were heated at 290° in vacuum. Similarly, samples of cotton were preheated at 290° in nitrogen (static) (C) and vacuum (D); then they were heated at 265° in nitrogen (static). Decomposition products would tend to accumulate to a greater degree in the samples initially and subsequently heated in nitrogen (static) than in

Table 2: — Effect of residual decomposition products on the formation of free radicals in heated cotton

Time of Heating, min.	Concentration of free radicals, arbitrary units, at heating conditions of:							
	Preheated 290° C.		Reheated 290° C.		Preheated 290° C.		Reheated 265° C.	
	N static	Vacuum	N static	Vacuum	N static	Vacuum	N static	
Corresponding samples								
	A	B	A	B	C	D	C	D
1	0.4	0.4	3.2	1.4	0.4	0.4	7.6	5.4
2	0.4	0.5	4.8	2.2	1.5	0.9	8.4	5.4
3	0.7	0.5	6.4	3.0	3.7	1.2	9.2	5.6
4	0.7	0.6	8.0	4.0	7.3	1.8	10.0	5.8
5	1.0	0.7	9.4	5.0	-----	2.3	10.6	5.8
6	1.1	0.8	11.0	6.2	-----	3.0	11.4	6.0
7	1.3	0.9	12.4	7.2	-----	3.6	12.2	6.2
8	1.5	1.0	13.8	8.4	-----	4.2	13.0	6.4
9	1.8	1.0	15.2	9.4	-----	4.9	13.6	6.5
10	2.0	1.1	16.6	10.6	-----	5.5	14.4	6.7

samples heated in vacuum. This is reflected in the yields of free radicals in the heated cottons. The apparent energy of activation for the formation of free radicals in purified cotton heated in nitrogen (static) was 33 kcal./mole; the energy for formation of radicals in cotton heated in vacuum was 57 kcal./mole.

The effects of decomposition products trapped in heated cotton are similar to the effects of additives on cotton on formation of free radicals. Additives, such as potassium bicarbonate, borax, sodium carbonate, and ammonium phosphate, lower the temperature at which decomposition of heated cotton, as measured by formation of free radicals, is initiated. The amount of residual char in thermolyzed cotton is greater for samples treated with additives than for untreated samples. However, the ESR spectra of free radicals trapped in the char from both treated and untreated cotton were the same in the temperature range from 250° to 350° C.

Exposure of the charred samples to oxygen at about 25° C. increased the intensity of the ESR spectra, in some cases as much as 200 percent. This increase in intensity of the ESR spectra of the trapped radicals could be almost completely removed by applying a vacuum to the sample, by flowing nitrogen through the sample, or by increasing the temperature of the sample to about 250° C. The line-width and shape of the ESR spectra of the trapped radicals were the same in both the presence and absence of oxygen. A change in the infrared spectra of the char was recorded in the 1,000 to 1,100 cm.<sup>-1</sup> region on the introduction of oxygen. The reactivities of thermally initiated free radicals in cotton, treated cottons, and their chars, as related to oxidation of and flame-proofing processes for cotton products, are discussed.

## REACTION OF COTTON CELLULOSE WITH PHOSPHORUS TRIHALIDE-DMF SYSTEMS AS AN EXPERIMENTAL APPROACH TO FLAME-RETARDANT FABRICS

by

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(Presented by Tyrone L. Vigo)

At room temperature cotton underwent rapid reaction with the addition product of phosphorus trichloride and dimethylformamide (DMF). This PCl<sub>3</sub>-DMF adduct is known to contain two moles of DMF per mole of phosphorus trichloride. The treatment was applied to cotton sateen to produce flame-retardant fabrics

having high phosphorus contents and moderate percentages of nitrogen. The effect of reaction time, adduct concentration, wash procedure, and durability of the cellulosic product to home launderings was investigated. A mechanism is proposed for the initial reaction of this adduct with the cotton and its subsequent chemical



behavior on the basis of elemental analyses and infrared spectra.

The reaction of the  $\text{PCl}_3$ -DMF adduct with cotton sateen was dependent on the solvent in which the adduct was dissolved, the concentration of the adduct used, and the reaction time. Of the solvents screened, chloroform and DMF were the most effective in causing reaction of the adduct with the cellulose. The latter was chosen in most cases, since it was also used as a pretreatment solvent (30 minutes soak time in all cases) to activate the fabric, and was the most effective one in minimizing strength losses due to the presence of free hydrochloric acid.

Large increases in the weight gain and in phosphorus and nitrogen contents of the treated fabrics, as well as in flame resistance, were observed on increasing the concentration of the adduct. Cotton sateen fabrics reacted for an hour with adduct concentrations of 1 to 15 percent (bath ratios used: 40 parts of solution per part of cellulose by weight) had weight gains of 3.5 to 18.2 percent (percent P = 0.9 to 3.8; percent N = 0.4 to 0.8) when subsequently washed with DMF, 5 percent aq. acetic acid (10 minutes), and briefly with tap water (1 minute) before air-drying.

The flame resistance increased greatly even during fabric treatment at low adduct concentrations, with 2 percent adduct treatment for 1 hr. producing a fabric having a char length of only 2.5 inches. This fabric possessed a 7.2 percent add-on, contained 1.23 P, and 0.56 percent N. Increasing the adduct concentration above 15 percent had no additional beneficial effect on improving the initial flame resistance of the fabric, but did moderately increase the phosphorus contents to levels as high as 5 percent.

Although the wash procedures used subsequent to adduct treatment had no noticeable effect on the resultant weight gain or phosphorus contents, they did have a marked influence on the resultant flammability of the fabrics and on the nitrogen and calcium contents obtained. Fabrics washed with DMF, 5 percent acetic acid, and briefly with tap water (hereafter called the acetic acid wash method) required much less adduct application to impart high flame resistance than fabrics washed briefly with DMF followed by tap water for 30 minutes (called the tap water wash). Sateen fabrics treated for an hour with 2-percent adduct, and then given the acetic wash, passed the vertical flame test (2.5 inches char length), while a similar treatment with 5 percent adduct, followed by a tap water wash, produced a fabric having a char length of 5.5 inches. Elemental analyses of the two fabrics were as follows: Acetic acid method: 1.23 percent P, 0.56

percent N, 0.06 percent Ca; tap water method: 2.49 percent P, 0.37 percent N, 0.36 percent Ca. The loss of nitrogen and moderate calcium uptake of the fabric washed in tap water suggests that the fabric forms a different derivative when first washed with water than when first given an acetic acid wash.

At a given adduct concentration, an increase in the reaction time resulted in an increase in add-on, and in phosphorus and nitrogen content, as well as a reduction in the flammability of the cotton fabrics. By utilizing the acetic acid wash procedure, reaction times were varied from 5 to 60 minutes at 2- and 5-percent concentrations of the adduct. The most rapid increase in the weight of the fabric was observed when the reaction time was increased from 5 to 15 minutes (irrespective of the adduct concentration used). A typical example is afforded by comparison of fabrics treated with 5-percent adduct for 5 and 15 minutes: the former had a weight gain of 6.5 percent, contained 1.34 percent P, 0.40 percent N, and gave a char length of 3.5 inches, while the latter had an add-on of 10.2 percent, contained 2.33 percent P, 0.57 percent N, and gave a char length of 3 inches. In terms of minimum reaction time and adduct concentrations, treatment with 2-percent adduct for an hour or 5 percent for 5 minutes was quite adequate in producing flame-retardant sateen fabrics (char length of less than 4 inches).

The durability of the flame-retardant cotton fabrics to standard home launderings (normal wash and dry cycles) was investigated. The fabrics subjected to laundering were previously reacted for an hour with 5- to 25-percent concentrations of the adduct in DMF or DMF-chloroform (used at adduct concentrations greater than 15 percent), and washed by both the acetic acid and tap water procedures. Because of the hydrolytic behavior of the fabrics, only those treated with adduct concentrations of 20 percent or greater had adequate flammability after 10 home launderings. Sateen fabric treated with 20-percent adduct in 20-percent  $\text{CHCl}_3$ -60 percent DMF passed the vertical flame test after 15 launderings (char length of 2.5 inches) and had 4.8 percent P, 0.3 percent N, 0.5 percent Cl, and 1.3 percent Ca. A fabric treated with 25 percent adduct in 16 percent  $\text{CHCl}_3$ -59 percent DMF passed the vertical flame test even after 20 home launderings (3.5 inches char length), and had 5.2 percent P, 0.3 percent N, 0.8 percent Cl, and 1.2 percent Ca. At this stage of development, fabrics treated with the adduct were assessed to have moderate durability to home launderings (10 to 20 cycles), and their initial flame resistance was excellent. Work is now in progress to reduce or eliminate the

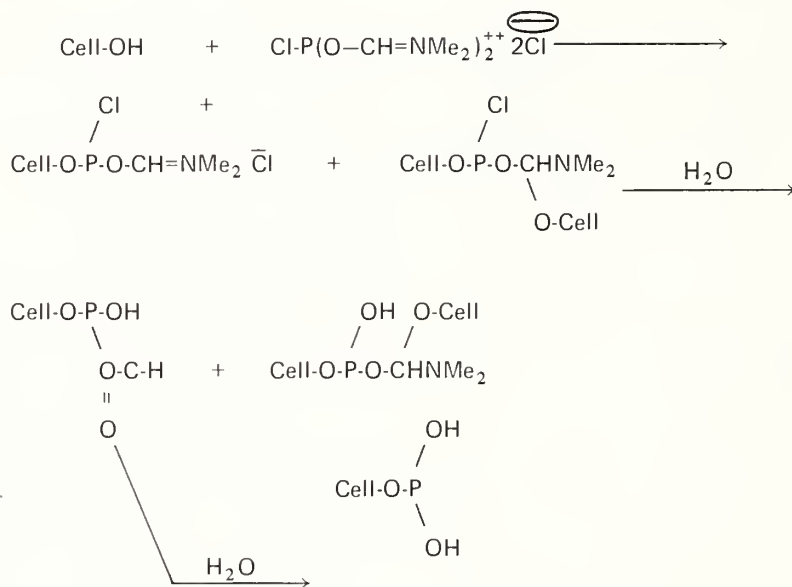
hydrolytic changes detrimental to the flame resistance of these fabrics.

Treatment with the adduct produced moderate increases (40° to 60°) in both the wet and dry wrinkle recovery of the sateen fabrics. The wet wrinkle recovery quickly reached a maximum with only 5-percent adduct treatment (224° compared with 168° for untreated sateen), while the conditioned wrinkle recovery reached a maximum with the 15 percent adduct treatment (230° compared with 183° for untreated sateen); reaction time had little effect on the wrinkle recovery at a given adduct concentration.

Tensile properties of the adduct-treated fabrics were adversely affected by increasing the adduct concentration, but unaffected by increasing the reaction time. For example, reaction with 5-percent adduct for times of 5 to 60 minutes produced a fabric having strength values (relative to untreated sateen) of 77 to 65 percent; treatment with 25 percent adduct in 16 percent  $\text{CHCl}_3$ -59 percent DMF for an hour reduced the strength retention to 33 percent of that of untreated fabric.

In an effort to elucidate the mechanism by which this adduct reacts initially with the cotton cellulose, and undergoes gradual changes during laundering, sateens were treated with 5- and 15-percent solutions of the adduct for 15 minutes, then washed by three different procedures: (1) DMF, then chloroform, (2) the acetic acid wash previously described, and (3) the tap water wash previously described. Elemental analyses for percent P, N, Cl, and Ca revealed that (1) percent P was unaffected by the wash procedure employed, (2) percent N decreased progressively from the  $\text{CHCl}_3$  wash to the acetic acid wash to the tap water wash, (3) percent Cl was only appreciable with the chloroform wash, (4) percent Ca was only appreciable with the tap water wash, and (5) the first four observations were true at either adduct concentration investigated. In terms of P/N and P/Cl ratios, fabrics treated with the adduct and given a nonaqueous ( $\text{CHCl}_3$ ) wash contained one P for every N and Cl atom.

A mechanism consistent for the reaction of the cellulose with the adduct and subsequent hydrolysis of the cellulosic product is as follows:



In addition to being consistent with the analyses found, this mechanism is also supported by the infrared spectra of the cellulosic product taken after subjection to each of the three aforementioned wash procedures. A progressive increase in the carbonyl absorption occurs when the

fabric is washed in aqueous media, particularly tap water; this may be attributed to production of the very labile formate ester of the phosphorylated cellulose depicted in the equations above.



# A NEW RAPID METHOD FOR THE DETERMINATION OF WATER IN THPC BASED FABRICS

by

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(Presented by R. J. Berni)

A method has been developed for the rapid analysis of water absorbed on cotton. A Varian Aerograph Model 1520 gas chromatograph with a thermal conductivity detector, a matrix temperature program unit, and 10-foot by 1/4-inch (100/120 mesh) Poropak T column was used. Acetone was selected as the solvent for extracting water from cotton; anhydrous methanol was used as an internal standard in the acetone.

Fabrics analyzed were desized, scoured, and bleached (80 x 80) printcloth weighing 3.4 ounces per square yard. Samples were prepared for analysis by using a wrinkle recovery testing die which provided 4 x 1.5 cm. samples weighing approximately 66 mg.

*Determination of standard curve for water analysis.* — A standard anhydrous acetone solution containing 10.89 mg. of methanol (MeOH) per ml of solution was prepared. Three ml. of this solution were added to 2-dram bottles fitted with rubber septum stoppers and then accurately weighed. Microliter aliquots of deionized water were added and the bottles reweighed to

determine amounts of water added. Some standard acetone-methanol solution was also placed in a stoppered bottle at the time of sample preparation and served as a blank. Microliter samples of each were chromatographed. Data obtained from the chromatogram are shown in table 1. Because of the similarity in shape of the water and methanol peaks, peak heights were selected for measurement. A ratio of water to methanol peak heights was determined. The  $\Delta$  value represents the difference in the ratios from the sample and the blank solution. A plot of the  $\Delta$  values vs. the weight ratios of water to methanol was linear. The least squares line through the experimental points can be expressed by the following equation.

$$\text{mg H}_2\text{O} = \frac{\text{mg. CH}_3\text{OH} [\Delta - 0.0003]}{1.071} \quad (1)$$

The line has a correlation coefficient of 0.999 and a standard error of estimate of 0.01.

Table 1: — GLC data for determination of standard curve for water analysis<sup>1</sup>

Added H <sub>2</sub> O mg	H <sub>2</sub> O	Peak height CH <sub>3</sub> OH	H <sub>2</sub> O/CH <sub>3</sub> OH	$\Delta$ <sup>2</sup>	mg H <sub>2</sub> O/CH <sub>3</sub> OH
0	8	106	.075	-----	-----
0.92	11	103	.106	.031	.028
2.51	17	107	.159	.084	.077
4.66	26	108	.241	.166	.143
9.76	40	106	.377	.302	.299
14.75	59	107	.551	.476	.451
19.59	76	106	.717	.642	.599
24.26	95	107	.888	.813	.742
34.35	103	86	1.198	1.123	1.051

<sup>1</sup> Acetone used as solvent containing 10.89 mg MeOH/ml of solution.

$$^2 \Delta = \left[ \left( \frac{\text{H}_2\text{O}}{\text{CH}_3\text{OH}} \right)_{\text{peak height sample}} - \left( \frac{\text{H}_2\text{O}}{\text{CH}_3\text{OH}} \right)_{\text{peak height blank}} \right]$$



*Determination of water present in cotton fabric.* — The current standard user for the determination of moisture in cotton<sup>1</sup> is accurate but too time consuming for use in a production line operation. In instances where the moisture content of the fabric before its modification affects the resulting fabric properties, the time in determining the moisture contents may be critical and costly. The standard method<sup>1</sup> lacks applicability when other volatiles are present. Since the glc peak heights of water are linearly related to the weights of water in solution, the determination of water in cotton fabric should depend only on the efficiency of extracting the water from the cotton by a solvent.

In a series of experiments known amounts of water were added to 30 mg. samples of cotton fabrics which contained their original 5.7 percent water. To these fabrics, enclosed in small bottles fitted with rubber septum was added 3 ml. of stock solution. After soaking the fabrics for one hour, each solution was chromatographed as described earlier. On an average 95 percent of all water present on the cotton was extractable and detected. A plot of the water detected vs. the water present yields a least square line that could be expressed by the following equation.

$$\text{mg H}_2\text{O present on cotton} = 0.468 + 1.01 (\text{mg. H}_2\text{O detected})$$

The line has a correlation coefficient of 0.999 and a standard error of estimate of 0.21.

A similar procedure was used to determine a standard curve for formaldehyde in the presence of methanol. The Porapak T column was also used to separate formaldehyde, water, methanol, and acetone from a mixture. A typical glc curve is shown in figure 1.

*Practical application of the method.* — Beninate and coworkers<sup>2</sup> previously postulated that moisture content (after drying and before ammonia curing of THPOH-padded fabrics) could adversely affect durability of the flame retardancy. Therefore, fabrics (80 x 80 print-cloth) were twice padded to 90 percent wet pickup with a THPOH solution, then dried at various times at 80° C. Results of both glc

analysis for water and formaldehyde and durability of flame retardancy properties are shown in table 2.

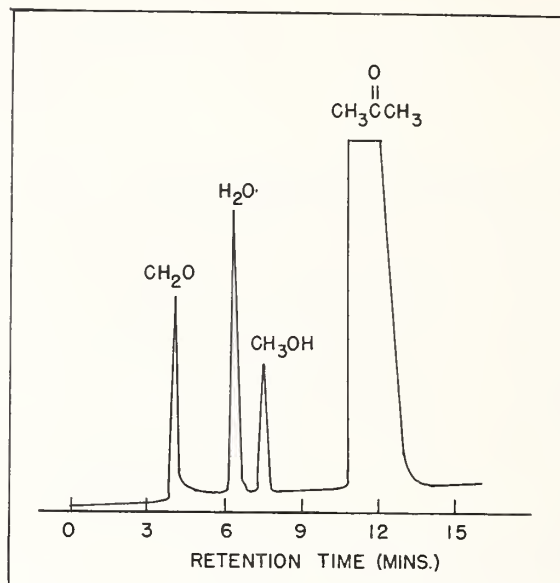


Figure 1. A typical chromatogram obtained on a Porapak T column for a mixture of formaldehyde, water, methanol, and acetone

Initially all fabrics show acceptable char lengths although add-ons were slightly reduced with no drying or a drying time of 1/2 minute, and were significantly reduced with drying times 10 minutes or longer at 80° C. With subsequent laundering, this initially reduced add-on was reflected in an overall decrease in flame-retardant properties as measured by char length. On the other hand, fabrics which had moisture contents about 3 to 15 percent gave add-on after curing of greater than 22 percent and good durability after 30 laundings.

These data indicate that with lightweight fabric and this particular treatment that durability can be affected by drying time. Underdrying or overdrying can result in a flame-retardant finish with poor durability to laundering.

<sup>1</sup>American Society for Testing and Materials, D2654, Philadelphia, Pa.

<sup>2</sup>Beninate, J. V., Boylston, E. K., Drake, G. L., Jr., and Reeves, W. A. Better flame resistant finish for cottons, Text. Ind. 131: 110-118. 1967

Table 2. Effect of drying time<sup>1</sup> on comparison of THPOH treated fabric and on durability of flame retardancy

Drying time (min.)	glc Analyses <sup>2</sup> of THPOH impregnated fabric			Properties of fabric after ammonia fixation of THPOH				
	H <sub>2</sub> O mg.	Per-cent <sup>3</sup>	CH <sub>2</sub> O mg.	Add-on Percent	Orig.	Char length (inches)		
						10 L.	20 L.	30 L.
0	32.05	33.9	6.63	21.7	3.7	BEL <sup>4</sup>	BEL	BEL
0.5	15.16	19.5	6.17	22.6	3.7	BEL	BEL	BEL
1.0	10.70	14.6	4.79	24.2	3.7	3.1	3.1	2.8
3.0	2.39	3.7	3.56	24.6	3.6	3.1	3.1	2.8
5.0	1.95	3.0	2.33	22.1	3.5	3.0	3.0	3.0
10.0	1.50	2.3	2.02	15.2	3.2	3.4	BEL	BEL
15.0	1.50	2.3	0.65	15.2	3.2	3.2	BEL	BEL
20.0	1.20	1.8	0.44	13.5	3.2	3.4	BEL	BEL
Control	3.57	5.4	-----	-----	-----	-----	-----	-----

<sup>1</sup>Cotton fabric twice padded with THPOH solution, dried at 80° C for indicated times, then ammonia cured.

<sup>2</sup>Gas-Liquid Chromatographic (glc) analyses of test samples (66 mg.) cut before ammonia curing. Char length determined on original treated fabric, after 10, 20, and 30 launderings (L).

<sup>3</sup>Percent =  $\frac{\text{wt. of water} \times 100}{\text{wt. of water} + \text{wt. of original dry cotton}}$ .

<sup>4</sup>BEL = burned entire length.

## LIQUID AMMONIA AND NONAQUEOUS SOLUTIONS OF AMMONIA IN PHOSPHORUS-BASED FLAME RETARDANTS

by

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(Presented by Timothy A. Calamari, Jr.)

Phosphorus-containing compounds are among the most efficient fire retardants currently available for cellulosic fibers and fabrics. The "THPOH"-gaseous ammonia finish developed at the Southern Regional Research Laboratory is one of the best presently available for lightweight fabric (4.0 oz. and less). The release of large quantities of formaldehyde during padding and drying operations and the use of large amounts of ammonia gas during curing have been drawbacks to its commercialization. Furthermore, conventional "THPOH" solutions tend to release hydrogen gas and could cause solution storage problems and processing difficulties.

Conventional "THPOH" solutions contain NaOH and THPC in a ratio of about 9/10 over a pH range of 7.2 to 7.8. When mole ratios of NaOH/THPC were varied from 1/10 to 9/10, the pH varied from 5.2 to 7.8. Durable finishes were formed when solutions having mole ratios of

NaOH/THPC of 5/10 and higher were padded on fabric prior to ammonia fixation. The most effective pH range was 6.3 to 7.8. Although the formaldehyde released during padding and curing was somewhat reduced by lower mole ratios of NaOH, the odor problem was still adverse.

Greater reductions in formaldehyde release were observed when the sodium sulfite was used in the preparation of "THPOH" instead of sodium hydroxide. When a mole ratio of Na<sub>2</sub>SO<sub>3</sub>/THPC of 5/10 was used, the formaldehyde released during padding and drying was greatly reduced. There did not appear to be any evolution of hydrogen gas during or after solution preparation. The pH of this solution was 5.2. When used in combination with a gaseous ammonia cure, this formulation produced a finish durable to 50 standard wash/dry cycles. The fabric so treated had an excellent hand. A convenient method of preparing sodium sulfite solutions consists of bubbling sulfur dioxide gas

into a caustic solution of the desired concentration until the pH is 10.2. This solution is then combined with a THPC stock solution to form the sulfite modified "THPOH."

In its present form the conventional "THPOH"-NH<sub>3</sub> process involves the use of large excess of ammonia gas during curing. Since many systems depend either in whole or in part upon the uniform penetration of ammonia gas into the "THPOH" sensitized fabric, the curing process also can be time consuming. It is necessary to carefully control the moisture present in the sensitized fabric before curing. Overdrying causes an excess loss of formaldehyde which results in a less reactive methylol phosphorus compound. Furthermore, some of the "THPOH" is converted to the inactive phosphine oxide when the pH of the solution is much above 7.0. Other methods of curing the "THPOH" sensitized fabric with ammonia were investigated with the aim of minimizing these problems. Liquid ammonia and nonaqueous solutions of ammonia which can be applied to fabric by padding were examined. Cold isopropanol was found to be a satisfactory solvent for ammonia. Both liquid ammonia and isopropanol solutions of ammonia were found to be satisfactory for this ammonia cure. By proper adjustment of processing variables, i.e., roll pressures, rate of travel through the bath, and so forth, the amount of ammonia applied to the sensitized fabric could be precisely controlled. Liquid ammonia and ammonia in isopropanol penetrate cotton fabric very rapidly. Since ammonia is applied from a pad bath, there is an almost instantaneous, uniform penetration of the fabric by ammonia and rapid fixation of flame retardant. The fabric can be quickly quenched with water or heated to remove the excess ammonia and then oxidized. If liquid ammonia is used, the additional advantage of increased fabric tensile strength due to ammonia mercerization is observed. Furthermore, when liquid ammonia

cures are used with either conventional or modified "THPOH" sensitized fabric, much greater latitude in drying can be used than with the gaseous cure.

The SRRL chainless mercerizer was found to be convenient and practical equipment for applying pad-bath ammonia cures to either conventional or modified "THPOH." It is well hooded and capable of treating fabric over a wide range of processing variables. When either conventional or sulfite modified "THPOH" sensitized sheeting was treated with either of these pad baths on the SRRL mercerizer, durable finishes with an excellent hand were obtained. It should be pointed out that fabric stiffness did not occur although the cure was carried out under constant tension, which normally causes fabric stiffness.

Most "THPOH"-NH<sub>3</sub> finishes require at least 3.0 percent bound phosphorus to provide satisfactory durability to washing. If the phosphorus content could be reduced by the inclusion of additional sources of nitrogen, the cost of the finish could be reduced. Several formulations containing either THP, urea, and formaldehyde, or "THPOH" and urea were studied. None of the formulations containing "THPOH" and urea produced a durable finish when cured with ammonia. Solutions containing mole ratios of THP/urea/CH<sub>2</sub>O of 2/1/2 and 3/2/3 produced durable finishes when used with a liquid ammonia cure. A solution having a 1/1/1 mole ratio did not. The addition of urea to the THP-formaldehyde system enables the phosphorus level to be reduced to 2.5 percent, while still providing good durability.

The use of sulfite modified "THPOH" and liquid ammonia cures should enhance the practical application of the "THPOH"-ammonia finish. Liquid ammonia curing of THP, urea, and formaldehyde in the proper mole ratios produces a durable finish with a reduced phosphorus content.

## APPLICATION OF THPOH-AMIDE FLAME RETARDANT TO COTTON FLANNELETTE

by

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(Presented by John V. Beninate)

The THPOH-amide flame retardant being developed at the Southern Regional Research Laboratory is based on tetrakis(hydroxymethyl) (phosphonium hydroxide (THPOH), urea, and trimethylolmelamine. In earlier work,

treating solutions of 30- to 35-percent total solids containing the three components in a molar ratio of 2:4:1 (THPOH:urea:methylolmelamine), when applied to cotton fabrics of 8 ounces per square yard or greater imparted



durable flame resistance along with good hand and minimal losses in breaking and tearing strength. Application of this flame retardant formulation to lightweight cotton flannelette also imparts good flame retardancy. In most instances, however, the hand of treated fabric is somewhat harsh and not satisfactory for use in children's sleepwear. The stringent requirements of the recently issued flammability standard for children's sleepwear have increased the difficulty of developing flame retardant treatments which are acceptable for application to cotton flannelette. Because of this, the Southern Regional Research Laboratory has engaged in research to develop formulations and processes which can be successfully applied to this type of fabric and conform to the requirements of the standard.

Throughout this study, all treatments were applied to a 100-percent cotton flannelette printed on a white background. Fabric weight was 4.1 oz./sq. yd.

Experiments were conducted to modify the THPOH-amide formulation by varying the molar ratio of the active components THPOH, urea, and methylolmelamine. Fabrics were treated with solutions varying in total solids of from 33 to 35 percent in which the molar ratio of components were 2:4:1 and 6:5:1 (THPOH:urea:methylolmelamine). The fabrics were processed by padding, drying at moderate tempera-

ture, curing at elevated temperature, and followed by washing.

The effect of incorporating THPC/THPOH solutions containing varying mole fractions of THPOH in the treating formulations was determined with respect to efficiency of add-on, durability of flame resistance, and the hand and other physical properties of treated fabrics. The pH of the pad bath had an effect on the efficiency of the reaction. In general pH's slightly below 7 produced the best results.

By decreasing the amount of trimethylolmelamine used in the formulation, the resulting fabrics had a better hand, less yellowing when subjected to chlorine bleach, and better strength retention. When adequate amounts of flame retardant were applied to flannel fabric, good flame retardancy resulted which was durable to over 50 laundry cycles.

All treated fabrics were subjected to an oxidizing treatment by padding with a solution containing 5 percent hydrogen peroxide and 1 percent sodium silicate followed by washing in hot water.

Short yardages of cotton flannelette were treated on a semipilot plant scale. The treated fabrics were evaluated with respect to flame resistance, durability of the finish to laundering, hand, and other physical properties, wash-wear ratings, and yellowing caused by chlorine bleaching.

SESSION V: William R. Martin, Jr., American Association of Textile Chemists and Colorists, Chairman

## PREVENTING CIGARETTE IGNITION OF MATTRESSES<sup>1</sup>

by

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(Presented by J. P. Neumeyer)

### ABSTRACT

In September 1971 the Department of Commerce announced a proposed standard for the flammability of mattresses. The standard requires the use of three lighted cigarettes placed at designated points on both bare mattresses and mattresses covered by two sheets. The selection of the cigarette test is based upon the conclusions by the Bureau of Standards that cigarettes are the prime source of ignition in bedding fires.

Current research efforts at the Southern Regional Research Laboratory (SRRL) consider two major approaches to minimize the potential

for the ignition of mattresses by cigarettes. These are: (1) Backcoating of the ticking with a polymer; (2) treatment of the cotton batting filler to make it flame and smolder resistant. The approaches are predicated upon the finding that smoldering combustion rather than flaming combustion ensues when cigarettes are used as the ignition source for mattresses.

The backcoating technique is designed as a means of preventing the cotton batting from reaching the critical temperature of about 400° C. at which smoldering combustion is induced; while the treatments of the cotton batting are

<sup>1</sup>This research is being conducted under a cooperative agreement with the National Cotton Batting Institute, Cotton Incorporated, and the U. S. Department of Agriculture.

aimed at altering the mechanism of smoldering combustion.

## INTRODUCTION

Before considering the processes occurring in the ignition and burning of cellulosic materials and the mechanisms by which these processes can be prevented, it would be well to review and define some pertinent terms used throughout this presentation. Pyrolysis is defined as the chemical decomposition of a material by the action of heat. Thermal degradation is often used synonymously with pyrolysis. Combustion is defined as the process of uniting a material chemically with oxygen at such a rapid rate as to produce heat and light. When the material undergoing combustion is gaseous in nature, the resulting heat and light generated are often manifest in the physical and visual phenomenon of flaming. When the combustion reaction occurs in a solid material, the physical phenomenon observed is referred to as glowing. Glowing combustion proceeds at a much slower rate than flaming combustion. Absence of either flaming or glowing does not mean that oxidation is not occurring, but that its rate is sufficiently slow, that no visible light is emitted. With this in mind it should also be noted that flames are some-

times observed in the burning of solid fuels. In this case flaming is evidence of rapid oxidation of the volatile gaseous products distilled from the solid fuels upon heating.

A cellulosic material will usually undergo flaming combustion when ignited by an open flame. Once a part of the material is consumed by the flaming reaction, the charred residue remaining often will continue to react through a solid-state glowing oxidation. Although "flaming" and "glowing" often appear to occur simultaneously, the two phenomena involve very different oxidation reactions.

Many cellulosic materials undergo smoldering combustion. Smoldering is defined as burning and smoking or wasting away by a slow and suppressed combustion without flame. Within the realm of this definition both gaseous and solid-state oxidation may occur. The "glowing" phenomenon is not excluded by this definition.

*Thermal energy balance.* — Several criteria related to ignition source, rate of heating, surface temperature, reaction rate and heat transfer environment must be satisfied before combustion can be achieved or sustained. Figure 1 illustrates a thermal energy balance for use in this discussion.

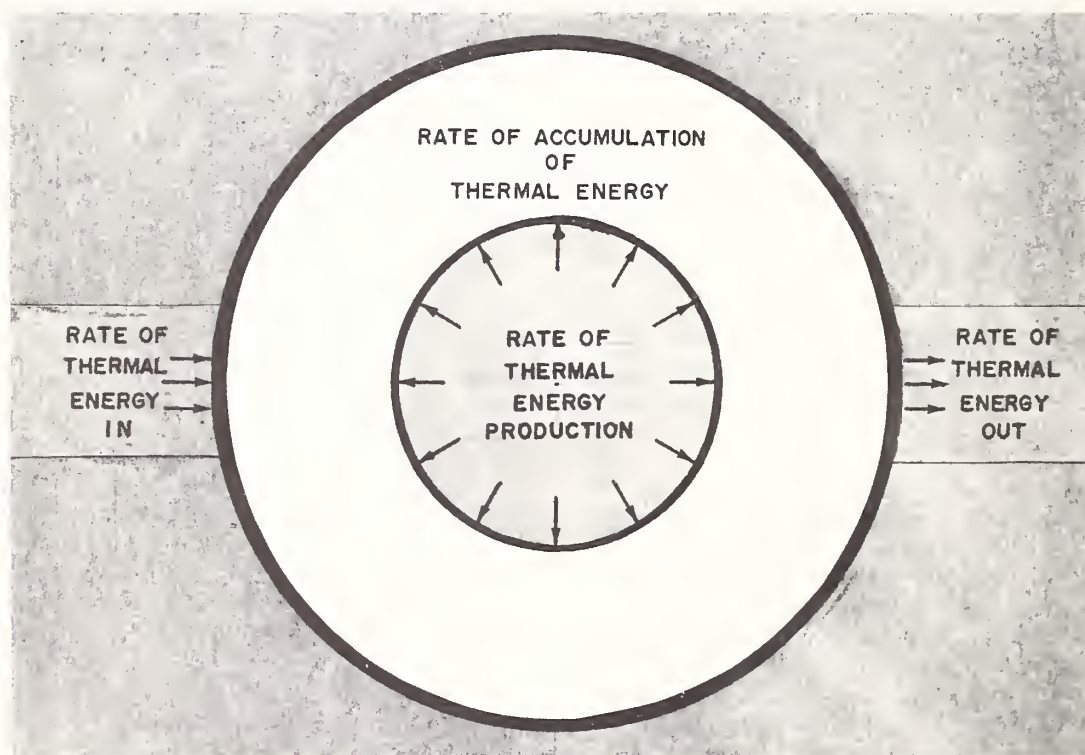


Figure 1. Thermal energy balance

The rate of energy transfer into the system is determined by the ignition source, heat transfer environment, and the thermal properties of the

material. Heat can be transferred to and through the material via conduction, convection, and radiation. The accumulation term reflects the



increase of thermal energy in the cellulosic material and relates the temperature, density, and heat capacity. As the temperature increases, the material produces energy through an exothermic combustion reaction. Higher temperatures, in turn, increase the rate of energy production. The rate of heat loss through and from the system is affected by conductive, convective, and radiative properties of both the material and the environment.

Obviously if the rate of heat loss from the system is small relative to the rate of energy input from the source, the system temperature will increase. Energy will be produced from the exothermic reaction at a faster rate and contribute to a further increase in temperature. A condition could be reached in which the combustion reaction could sustain itself even if the source of ignition were removed. Under these circumstances combustion would continue until either the fuel supply was exhausted or until a large increase in energy transfer from the system occurred. Self-sustained combustion is a normal occurrence in the burning of cellulosic materials.

In vertical flame testing, a high rate of energy input is sustained over a relatively short period of time. When testing an untreated cotton fabric, the material will accumulate energy and increase in temperature, with a simultaneous increase in the production of energy resulting from the exothermic oxidation of gaseous and solid pyrolysis products. Flaming will undoubtedly occur. Self-sustained combustion will usually continue after the source of heat is removed. The addition of a suitable flame retardant does not alter the rate of energy transfer to or from the tested fabric, nor does it appreciably affect its physical properties. Its effectiveness is measured primarily by its action on the pyrolysis mechanism resulting in reduced rates of the exothermic combustion reactions.

When vertical flame testing a batting sample, a considerably different process is apparent. The high rate of heating over a relatively short time does not appreciably heat the batting structure, primarily due to its good insulative properties. Its thermal response is slow, thus short heating periods only heat the outer webs of the batt. Nevertheless, untreated cotton batting will burn vigorously when vertically tested. The addition of a flame retardant alters the reaction mechanism to produce less energy, and the batting structure easily passes a vertical flame test. It should be noted that consistently lower add-ons of flame retardants are sufficient for the batting to pass a vertical flame test than are required for a fabric. This is a result of (1) the heated area of the batt is located primarily along the outer webs where heat transfer to the environment is

large due to high porosity and convective currents; and (2) the apparent density of the batting is low relative to that of a fabric, and thus the energy produced per unit volume by the reaction is not as concentrated as in a fabric.

Now let us examine what transpires if the environment is altered to change the rate of energy removal from the cellulosic material. Consider the effect of heating a batting structure at a point internal to the webs. The good insulative properties of the batt inhibits the loss of heat from the structure; its temperature increases; exothermic combustion ensues; the combustion reaction contributes to even further increase in temperature; ultimately the material undergoes self-sustained smoldering combustion. Where such conditions exist products that easily pass the vertical flame test can be consumed by smoldering combustion. Figure 2 confirms that a piece of THPOH-treated cotton fabric, which was self-extinguishing and had no after glow when vertically flame tested, could be completely consumed by smoldering combustion after being ignited by a cigarette between two fiber glass batts. These findings illustrate the critical nature of the heat transfer environment.

In mattresses containing cotton batting, combustion is usually of the smoldering type. When subjected to a slow and continuous heat source, such as a cigarette, the insulative properties play a significant role in the initiation and sustainment of smoldering combustion. In order to study cigarette ignition of smoldering combustion, a batt of fiber glass material was used to simulate the filling in a mattress structure. Eight thermocouples were placed at positions as shown in figure 3 to obtain a surface temperature profile along the length of a burning cigarette. Figure 4 illustrates a typical profile. Notice that the temperature at each point passes through a maximum and that the peaks not only become higher but, more significantly, broader as the burning progresses. This shows that a given temperature will be sustained over a longer period of time toward the end of the burning process. Thus, the exothermic oxidation reaction that follows will have more time to raise the local temperature above the critical temperature of about 400° C. (5), at which smoldering combustion becomes self-sustaining. The profiles also explain why the mattress ignitions from cigarette testing are usually observed to occur in the late stages of the cigarette burning process. The same effect was apparent when filling material was treated with aluminum trihydrate, an energy absorbing compound. The length of the cigarette burn before ignition increased with increasing add-on of the hydrate.





Figure 2. THPOH treated fabric consumed by smoldering combustion

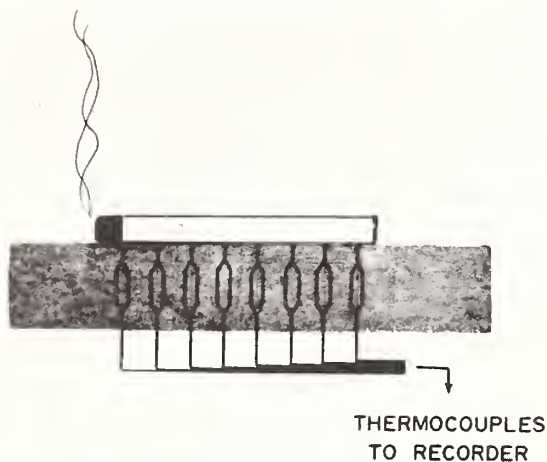


Figure 3. Thermocouple location for cigarette temperature profile

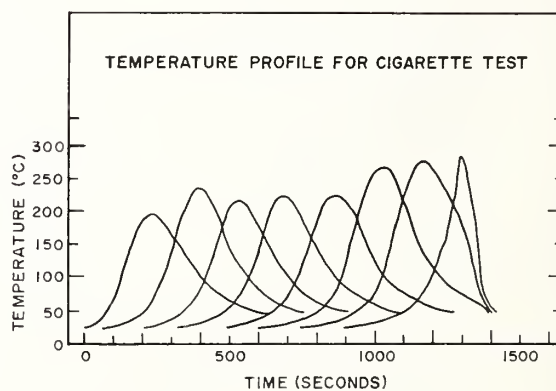


Figure 4. Typical temperature profile for a burning cigarette

Based on the above findings two alternatives for preventing cigarette ignition of smoldering combustion in mattresses appeared promising:

- (1) Treat the filling materials to alter the

mechanisms of both pyrolysis and exothermic oxidation of the pyrolysis products. By doing so the rate of thermal energy released would be suf-

- ficiently decreased so that the critical temperature would not be attained.
- (2) Effect a shield or thermal barrier to prevent the heat of the ignition source from raising the temperature of the filling materials. Doing so would inhibit the pyrolysis and subsequent exothermic oxidation sufficiently so that the critical temperature is not reached.

### TREATING THE FILLING MATERIALS

**DTA-TGA-DTG.** — Differential thermal analysis (DTA) is a thermal technique in which the heat effects associated with physical or chemical changes are measured. The procedure consists of heating the sample and an inert reference material at a programmed rate and simultaneously observing the temperature differential between the two (6, 8).

Figure 5 demonstrates the thermal effects of heating scoured and bleached cotton in various atmospheres. It is observed that only endothermic processes occur in an inert nitrogen atmosphere. These energy absorbing processes result from the thermal degradation of cellulose and the distillation of the volatile products. When heated in air, an entirely different thermogram results. Two exothermic peaks are observed. The first exotherm corresponds to the oxidation of the volatile pyrolysis products. If the fuel-oxygen mixture is rich enough, flaming will occur. The second exotherm results from the oxidation of the carbonaceous char. If this reaction occurs at a sufficiently high rate, glowing is observed. The ignition temperature for self-sustained smoldering combustion in scoured and bleached cotton was found to be 412° C. (5), which is close to the onset temperature of the second exotherm. Notice the effect of decreasing oxygen supply on the exothermic behavior during heating. In a mixture of 50 percent air and 50 percent nitrogen, the solid-state reaction appears to have been hindered to a greater extent than the oxidation of the volatile pyrolysis products. This is to be expected since there is a more favorable reaction environment in the vapor regime than at the solid surface. Exothermic activity is evident with as low as 1 percent oxygen. Thus even at the very lowest oxygen levels, combustion is likely to be self-sustaining if the heat losses are minimal.

Another important technique in studying thermal degradation is thermogravimetric analysis (TGA) (2). In TGA the weight of the sample is continuously monitored as it is heated at a programmed rate. The resultant weight change vs. temperature plot provides information on the thermal stability and composition of the original sample, intermediate compounds and the residue.

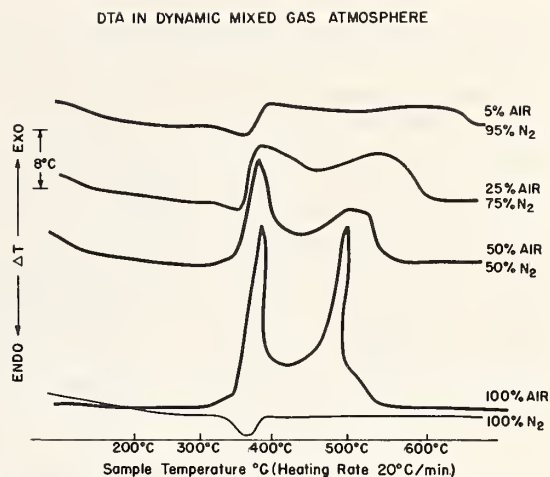


Figure 5. Thermograms for scoured and bleached cotton in various atmospheres

Figure 6 shows the TGA curves obtained from the heating of scoured and bleached untreated cotton in two different atmospheres. In both cases almost 90 percent of the weight loss occurs in a relatively small temperature span beginning about 300° C. Differentiating the TGA curve in time, and plotting the derivative as a function of time or temperature, results in the differential thermogravimetric curve (DTG) (1). In DTG a series of peaks are obtained, instead of the stepwise curve, in which the areas under the peaks are proportional to the total weight change of the sample. Peaks in the DTG curve correspond to maximum rates of weight losses. In an inert nitrogen atmosphere only one peak is observed, corresponding to the large weight loss due to thermal degradation. This was seen to be an endothermic process by DTA. In a 50-50 nitrogen-air mixture, two peaks are observed. The first is associated with the weight loss due to pyrolysis. The second, which might have gone unobserved without DTG, is associated with the solid-state combustion of the carbonaceous char remaining after pyrolysis. DTA demonstrated both of these reactions to be exothermic in air. The peak temperature of the second reaction, 556° C., corresponds closely with that observed in the DTA of carbon black, more evidence that the reaction is the oxidation of the solid char. Note that the presence of oxygen significantly increased the rate of the first reaction by 1.25 mg./min.

Figure 7 illustrates the effect of different concentrations of phosphoric acid on the combustion of scoured and bleached cotton. Phosphoric acid behaves as a Lewis acid flame retardant. As the concentration is increased the onset temperature of pyrolysis decreases. Increasing the add-on from 1- to 10-percent lowers

the peak of the first exotherm 43° C. Concurrently the peak of the second exotherm is raised 18° C. The rate of energy released is decreased in both the first and second exotherms. This is evidenced by a broadening of the peaks and a lowering of their amplitudes. Examining the TGA and DTG curves (figure 8) for the 5- and 10-percent samples confirm the effect of increasing add-on upon reaction rate. The weight loss associated with the solid-state oxidation is shifted higher in temperature. Again the peaks are broader and exhibit decreased amplitudes. The rate of weight loss for the first peak is decreased from 2.2 to 1.23 mg./min. and the second peak from 0.41 to 0.35 mg./min.

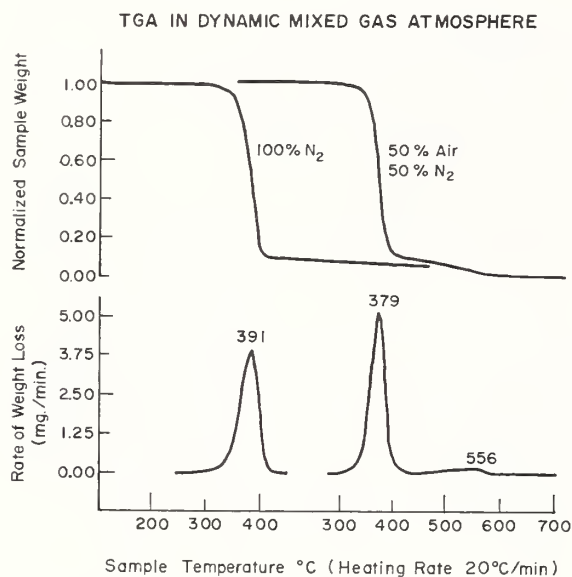


Figure 6. Thermogravimetric curves for scoured and bleached cotton in different atmospheres

In general, phosphorus containing compounds inhibit both the first and second oxidation reactions associated with combustion of cellulosic materials. Their value for hindering the first reaction is explained as an influence on the pyrolysis mechanism. Little is known about the details of their effectiveness on the second reaction. One theory is that the polyacid (a viscous, sticky, melt-type substance) formed on decomposition of phosphorus compounds provides a physical barrier surrounding the combusting fibers (7). Other theory envisions a catalytic altering of the solid-phase oxidation process (7). If the former is controlling, then the activity which contributes to the formation of a barrier must effectively occur at temperatures below that of the second reaction. If the latter controls, it would be active during the solid-state oxidation.

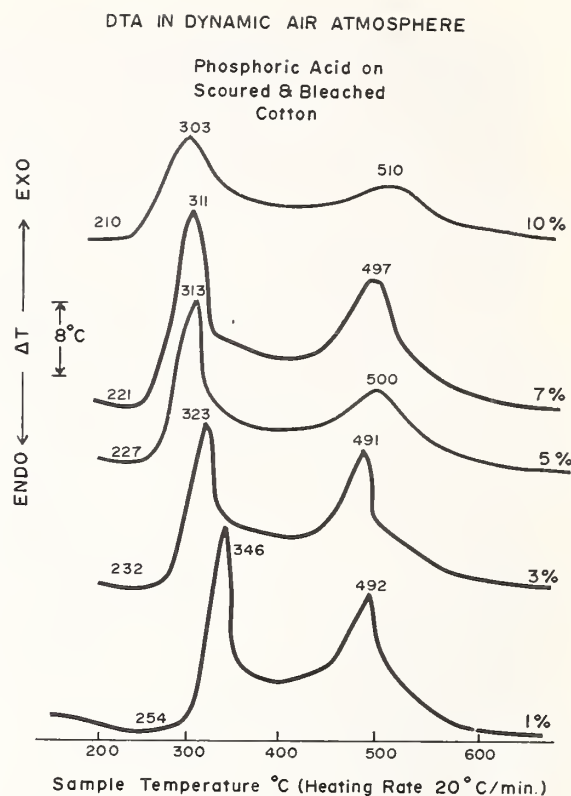


Figure 7. Effect of phosphoric acid concentration upon the shape of the DTA curves

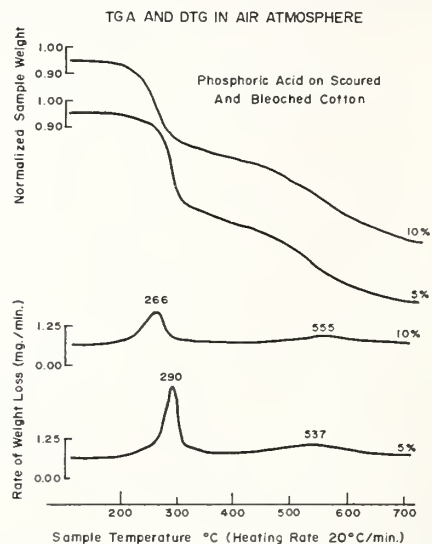


Figure 8. Effect of 5 and 10 percent phosphoric acid concentration on TGA and DTG curves

*Phosphoric acid, urea-phosphate, and THPC-amide treatments.* — Cotton batting raw-stock treated with a series of phosphoric acid, urea-phosphate and THPC-amide formulations was evaluated to determine the add-on necessary



to provide protection against cigarette ignition. Each of these systems reacts as a Lewis acid being capable of catalytic activity which changes both the course and speed of the combustion reaction (10). The rawstock was immersed and padded to about 100 percent wet pickup, dried and then garnetted into batts consisting of 20 webs. The batts were then used as filling material in constructing mini-mattresses which were in turn tested for ignition along the taped edge by both one and two cigarettes (figure 9). The results of these tests are presented in tables 1, 2, and 3. The letters I and N represent ignition and no-ignition, respectively. The proposed mattress standard is a go- no-go test. Consequently, it is unsuitable for rating performance. For research products where level of performance needs to be evaluated, two cigarettes side by side have been used to determine how much the performance exceeds the minimum needed to pass the standard.

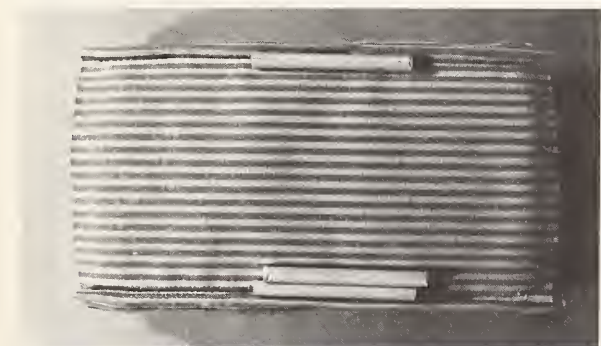


Figure 9. Mini-mattress structure for cigarette testing

Table 1. Cigarette testing mini-mattress structure

Phosphoric acid				
Percent add-on	P content	N content	Single cigarette	Double cigarette
5.5	1.58 pct.	—	I	I
9.5	2.36	—	I	—
15.3	3.49	—	I	—
21.4	4.10	—	N	I
27.0	6.56	—	N	I
39.9	9.20	—	N	N

For the phosphoric acid treatments, 4.1 percent phosphorus was required to pass the single cigarette test and 9.2 percent was needed for the two cigarette test. In both cases the total add-on was unfeasibly high and the filling material underwent excessive acid degradation. In the urea-phosphate treatments less phosphorus was required, 2.52 percent, with the assistance of 8.36 percent nitrogen. The total add-on required was higher than for phosphoric acid and considerable degradation still occurred.

The THPC-amide treated batting passed the single cigarette test with as little as 1.59 percent P and 5.27 percent N. Again the total add-on was unfeasibly high, and excessive degradation was evident. Even with as high as 54 percent total add-on, the structure continued to fail the two cigarette test.

Table 2. Cigarette testing mini-mattress structure

Urea phosphate			Single cigarette	Double cigarette
Percent add-on	P content	N content		
3.83	0.66 pct.	2.48 pct.	I	—
9.95	1.39	4.54	I	—
15.3	1.85	6.05	I	—
22.8	1.90	7.41	I	—
29.5	2.52	8.36	N	I
36.3	2.63	9.59	N	I

Table 3. Cigarette testing mini-mattress structure

THPC-amide			Single cigarette	Double cigarette
Percent add-on	P content	N content		
	7.5	21.5		
10.9	0.71 pct.	2.45 pct.	I	I
20.0	1.21	3.80	I	I
31.8	1.59	5.27	N	I
43.2	1.77	5.85	N	I
54.0	2.21	8.03	N	I

Differential scanning calorimetry (DSC) showed that the heat of the first reaction decreased with increased phosphoric acid add-on and increased with increased urea-phosphate add-on. Obviously the treatments were not providing protection solely by diluting the reaction to decrease the net amount of energy released. It is hypothesized that, in addition to decreasing the reaction rate through the usual Lewis acid mechanism, the viscous film forming polyphosphoric acid (or phosphorus polymer formed on heating) was available at the higher add-ons to sufficiently coat the fibers and thus drastically inhibit the rate of both the first and second reactions. This effect should be more evident in the second reaction where oxidation occurs on the surface of the charred fibers since a coating film would slow down or prevent oxygen chemisorption into the reacting layer of the carbonaceous char.

*Coating treatment for filling materials.* — The preceding results indicated that treating the filling materials with classical flame retardants to prevent cigarette ignition could not be expected to inhibit smoldering combustion. The film

hypothesis appeared promising so efforts were concentrated in that direction.

Intumescent agents produce a nonflammable multicellular insulative barrier when exposed to heat. By treating the filling materials with an intumescent, heat and mass transfer might be sufficiently inhibited to provide protection from cigarette ignition. The particular formulation used in these studies included a film forming latex to bind the water insoluble ingredients to the cellulose and had to be applied via the Cotton Flote Spray equipment (3, 4). As little as 10-percent add-on was needed to pass a single cigarette test, 13.5 percent passed the two sheet test (11), and 32.5 percent passed a two cigarette test (table 4).

Table 4. Cigarette testing mini-mattress structure

Percent add-on	Single cigarette	Two sheet	Double cigarette
Intumescent agent			
10.0	N	I	I
13.5	N	N	I
27.7	N	N	I
32.5	N	—	N
36.6	N	—	N
Borax:boric acid 7:3			
4.5	N	I	I
11.8	N	—	N
16.2	N	—	N

Borax/boric acid mixtures, although by definition are not intumescent, are known to swell into a frothy mass on heating, lose the waters of crystallization, and fuse into a clear melt. As little as 4.5 percent total add-on of borax/boric acid passed the single cigarette test. Only 11.8 percent was required for two cigarettes. There is no doubt that both of these two systems provided considerably more protection against cigarette ignition than any of the Lewis acid flame retardant treatments used.

Examining the TGA-DTG curves (fig. 10) for cotton batting treated with the intumescent agent shows that the onset temperature of pyrolysis is not lowered as when treated with Lewis acid flame retardants. The rate of the first reaction decreases from 1.52 to 0.92 mg./min. with increasing add-on from 13.5 to 32.5 percent. The maximum rate of weight loss occurs about 315° C. in each case. The rate of the second reaction decreases from 0.24 to 0.16 mg./min. Its maximum rate occurs at about 500° C.

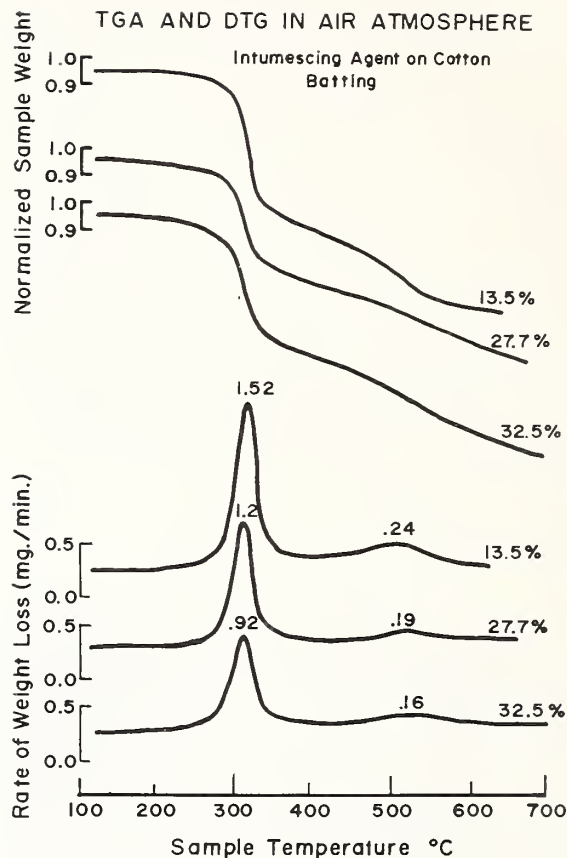


Figure 10. Effect of different concentrations of intumescent agent on the TGA and DTG curves of cotton batting

The TGA-DTG curves for the borax/boric acid treatments (fig. 11) demonstrate why these treatments are so effective. The first and second reactions are significantly reduced by as little as 4.5 percent add-on. The maximum rate of the first reaction decreases from 0.98 to 0.78 mg./min. as the add-on increases from 4.5 to 16.2 percent. The maximum rate of the second reaction decreases from 0.26 to 0.12 mg./min. Of considerable importance is that the maximum rate of pyrolysis occurs at 343° C., 28° C. higher than for the intumescent treatment. There appears to be some increasing activity occurring about 600° C. DTA shows this to be exothermic, however, it occurs at a temperature too high to affect cigarette ignition.

In figure 12 TGA-DTG curves for phosphoric-acid, intumescent and borax/boric acid systems are compared. Three treatments of approximately the same add-on were chosen. The curves are consistent with results obtained from cigarette testing mini-mattress structures which ranked the effectiveness of three systems.



It is obvious that the borax/boric acid system is most effective in reducing the reaction rates of the first and second reactions. It is also apparent that the temperature of maximum reaction rate is important. The instrument system is more effective than phosphoric acid primarily because the rate of the first reaction peaks about 50° C. higher. In the borax/boric acid treatment not only are the rates minimized but the first reaction peaks at 343° C., 28° C. higher than the intumescent treatment and 78° C. higher than the phosphoric acid treatment.

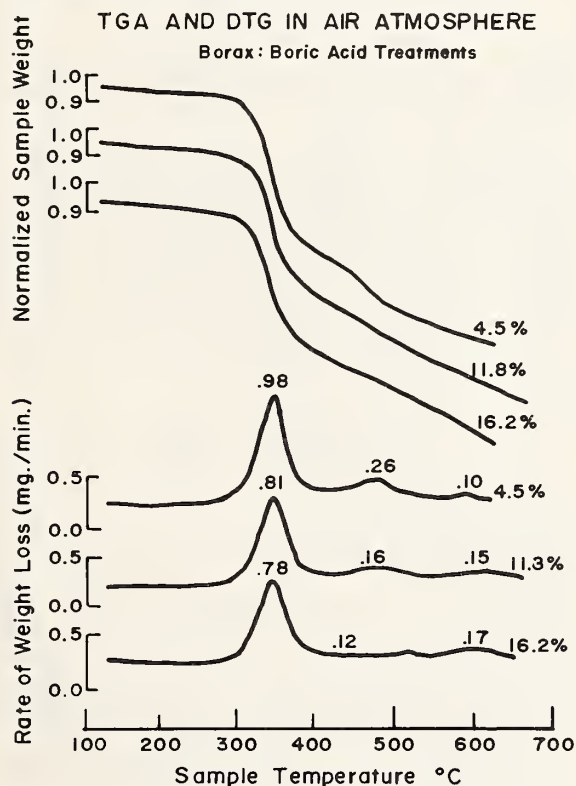


Figure 11. Effect of different concentrations of borax-boric acid on the TGA and DTG curves of cotton batting

While the borax/boric acid and intumescent treatments used in this work are not necessarily the optimum systems, they do indicate which types should be investigated. That is, those that decrease the rates of the two combustion reactions without lowering the pyrolysis temperature.

#### THERMAL BARRIER APPROACH

The use of thermal shield or barrier can be effective in inhibiting the heat of the ignition source from raising the temperature of the filling materials. As long as the filling temperature is prevented from reaching the critical temperature of about 400° C., self-sustained smoldering combustion should not occur.

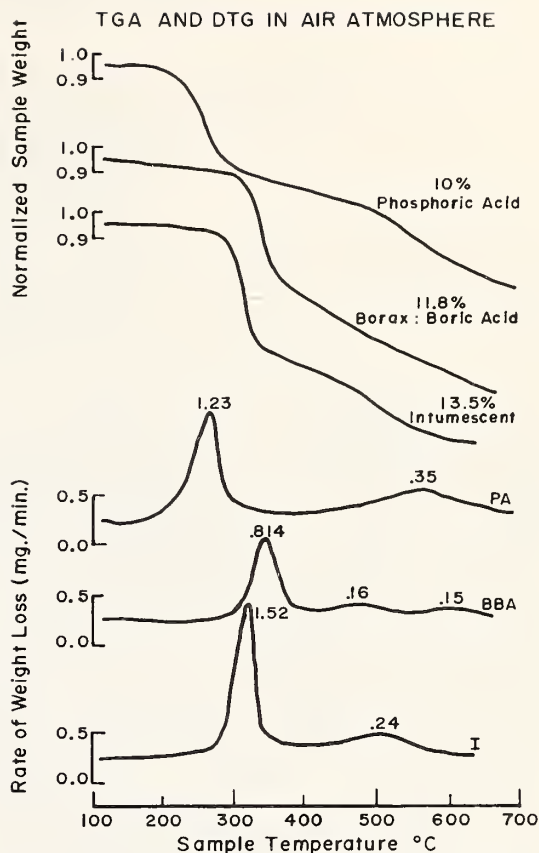


Figure 12. Comparison of TGA and DTG curves for cotton batting treated with phosphoric acid, borax-boric acid, and intumescent agent

*Backcoating the ticking.* — Another approach for preventing heat transfer to the filling material is polymer backcoating the mattress ticking. Some backcoating is presently being done commercially as a means of maintaining the ticking weight at lowered cost. This technique, therefore, should not require major changes in ticking manufacturing processes or mattress construction. For a backcoating to be effective it must act as a heat sink. It can do so by increasing the effective heat capacity of the ticking, absorb energy by endothermic melting and degradation, or it can operate by increasing the effective thermal conductivity of the ticking.

Eight different polymer systems have been evaluated for their effectiveness as backcoating agents for mattress tickings. Each was subjected to single and double cigarette testing in the mini-mattress configuration. Although these particular tests are of the go, no-go type, the eight systems tested could be classified into three broad categories as shown in table 5. The ratings are based on the add-on required for preventing cigarette ignition.



Table 5. Cigarette testing mini-mattress structure

Performance	Polymer backcoating	Percent add-on required	
		Single	Double
Good	Polyvinyl Acrylate	7.9	7.9
	Styrene-butadiene	7.1	17.4
Fair	Phosphorylated vinyl chloride	9.6	26.5
	Ethylene-polyvinyl chloride	9.9	22.0
	Polyvinyl acetate-acrylate-maleate	11.5	18.1
Poor	Polyvinyl acetate	18.1	18.1
	Polyurethane	18.4	29.6
	Polystyrene	>17.4	>17.4

Polyvinyl-acrylate and styrene-butadiene rated as the best evaluated while polyvinyl acetate, polyurethane and polystyrene were poor. The add-on levels required for the better systems do not present any process difficulties.

Properly selected additives used as fillers might permit a reduction in the polymer add-on required. To evaluate this premise aluminum-trihydrate, which is capable of absorbing approximately 240 calories per gram, was added to the treating formulations. No measurable protection against cigarette ignition was found. On the other hand, the addition of 1 to 2 percent aluminum pigment contributed some protection in addition to that observed for the polymer alone. While no quantitative measures of thermal conductivity have been made, literature data indicate that the polymer film is providing the major part of thermal conductivity and that small additions of metallic powders do not appreciably increase the polymer's thermal conductivity (9). It is probable that the value of the aluminum powder filler results from an increase in the effective heat capacity of the ticking as well as from reflective properties.

All of these systems are presently undergoing further evaluation with the temperature profile equipment described in figure 3 in an attempt to determine a more quantitative representation of their value as backcoating agents.

### CONCLUSIONS

To date this research has indicated that the classical approach to flame retardance via a Lewis-acid mechanism is not well suited for the prevention of smoldering combustion in mattress filling materials. While such treatments decrease the rate of combustion, they also undesirably lower the pyrolysis temperature and provide more fuel for the smoldering reaction. Intumescent and borax/boric acid systems, on the other hand, have proved to be effective. Both of these systems have superior coating properties which contribute to an inhibition of heat and mass transfer to the fibers. Thus, the

combustion reaction rates are significantly decreased without corresponding large decreases in pyrolysis temperature.

Another promising approach is polymer backcoating the mattress ticking. Eight different polymer systems have been evaluated. Polyvinyl acrylate and styrene butadiene rated as the best tested. While most of the available protection can be attributed to the polymer, as little as 1 to 2 percent aluminum pigment contributed some additional protection.

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# AMMONIA FIXATION OF THPOH FLAME RETARDANT IN A CONTINUOUS PROCESS

by

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Variables inherent in gaseous ammoniation of cotton impregnated with aqueous THPOH solutions were studied for both static and dynamic fabric substrates. Variables studied include ammonia gas flow rates, fabric and chamber temperatures, duration of ammoniation, fabric speed and time required for insolubilization of the flame retardant.

From information gained in the study of ammoniation variables, an apparatus for rapid and uniform delivery of ammonia gas to THPOH impregnated fabric on a continuous basis was designed, constructed, and evaluated as a stage of a continuous process for flame-retarding cotton.

## INTRODUCTION

The value of tetrakis(hydroxymethyl)phosphonium chloride (THPC), as a flame retardant for cotton textiles was first recognized in a study of the physical and chemical properties of aminized cotton<sup>1</sup>. Cotton containing 0.6 to 7 percent amino nitrogen and 1 percent phosphorus from THPC was shown to resist combustion, even after 2.5 hour boil in an aqueous solution containing soap and sodium carbonate. The principals established in this research lay the foundation for development of a number of flame-retardant treatments for cotton, culminating in the THPOH-NH<sub>3</sub> process of Beninate, Boylston, Drake, and Reeves<sup>2</sup>.

The technique involved in applying the THPOH-NH<sub>3</sub> flame retardant to textiles involves simply impregnation of the fabric with aqueous THPC neutralized to a pH of 7.0 to 7.5, predrying to 10- to 20-percent moisture, exposure of the textile to ammonia gas and subsequently washing and drying the treated material. Recently post-treatments of flame retardants derived from THPC with oxidizing chemicals have provided benefits above those

gained from the original treatment of the goods<sup>3,4</sup>. Such improvements include greater initial flame retardancy, elimination of unpleasant odors in the finished goods, and restoration of original fabric whiteness.

## RESULTS AND DISCUSSION

The improvements gained for the THPOH-NH<sub>3</sub> flame retardant through addition of an oxidation step to the process suggest that other areas for improvement may also exist. A study was thus undertaken to determine the source, magnitude, and effects of variables in the finishing process. Primary emphasis in this study is given to the stage of the process involving fixation of THPOH within the cellulose substrate through treatment with gaseous ammonia. Other process stages are considered on a "help or hinderance" basis, in terms of both their individual merit and their effect on the ammoniation stage.

*Ammoniation of static fabric substrates.* — In an effort to alleviate some of the problems inherent with diffusion controlled ammoniation, a bench-scale chamber was designed and constructed to effect forced ammoniation of fabric samples. With this technique all of the ammonia is made to pass through the fabric sample, thus effecting fixation of the THPOH while having full control of the ammonia gas. This technique offered possibilities for process improvements such as improved efficiency in terms of ammonia consumption, control of process odors, increased production rates through controlled transport of ammonia to the fabric, multiple fabric treatment, and additional advantages related to economics and ecology.

*Forced ammoniation variables.* — In forced ammoniation of static THPOH-impregnated substrates, there are three variables of immediate interest. These are temperature of the ammonia-

<sup>1</sup>Reeves, W. A., McMillan, O. J., Jr., and Guthrie, J. D. Textile Res. Jour. 23: 527. 1953.

<sup>2</sup>Beninate, J. V., Boylston, E. K., Drake, G. L., Jr., and Reeves, W. A. U. S. Patent No. 3,607,356 (September 21, 1971).

<sup>3</sup>Daigle, D. J., Reeves, W. A., and Beninate, J. V. Jour. Fire Flammability 1: 178. 1970.

<sup>4</sup>Hendrix, J. E., Beninate, J. F., Drake, G. L., Jr., and Reeves, W. A. The value of post-oxidative treatment of the THPOH-NH<sub>3</sub> cure flame retardant. To be published in Jour. Appl. Polymer Sci.



tion environment and fabric substrate, moisture content of the substrate, and flow rate of the ammonia gas. Each of these variables can conceivably affect the quality and efficiency of the insolubilization process.

The insolubilization of THPOH with ammonia is a net exothermic process, with heat being produced primarily from solvation of ammonia by moisture in the substrate and the condensation polymerization, respectively. During the insolubilization process, heat generated is dispersed through convective cooling by the dynamic ammonia gas and utilized in azeotroping water from the substrate with ammonia. These cooling effects result in a rapid decrease in fabric temperature after the polymerization begins to subside. Were these cooling effects not operative, one might encounter problems relating to heat buildup during the insolubilization process. As long as fabric temperatures remain moderate (i.e. less than about 100° C.), heat buildup presents no particular problems to the forced ammoniation process.

In the diffusion controlled process described by Drake<sup>5</sup>, the fabric is dried to 10- to 20-percent moisture content before exposure to gaseous NH<sub>3</sub>. Drying stages are costly in terms of process economics, however, and should be utilized only when they are absolutely essential. Thus effects of drying to reduced moisture contents before ammoniation of THPOH impregnated fabrics was investigated. Results of this study indicate that initial flame retardancy of the samples is slightly greater for pre-dried samples than for samples ammoniated in the wet state. The wet ammoniated samples also had a much better hand than the predried samples. Furthermore, if the substrate is overdried, a drastic reduction in flame retardancy occurs.

Anhydrous ammonia is a relatively inexpensive commodity, approximately \$0.03 per lb.<sup>6</sup>, but not so inexpensive that the quantity used can be ignored. Wasted ammonia would also present ecological problems. Since the forced ammoniation technique requires that all of the ammonia used pass through the fabric, it was reasoned that if just that amount of ammonia necessary for efficient insolubilization of the THPOH be brought to the fabric then ammonia waste would be minimized. At very low NH<sub>3</sub> flow rates, maximum flame retardancy is attained after about 3 minutes ammoniation time, which based on stoichiometry of the reaction represents about a two-fold excess. Taking into

consideration the large amounts of water retained by the substrate and the ammonia it retains through salvation, near to theoretical consumption begins to be realized.

*Ammoniation of dynamic substrate.* — Studies to this point indicated forced ammoniation to be a potential commercializable technique for insolubilizing THPC-based flame retardants in the cellulose substrate matrix. A semi-scale module for ammoniating fabric on a continuous basis was thus designed, constructed, and evaluated at "bench top". The module allows fabric to pass through the ammoniation chamber while a positive pressure of ammonia gas is maintained below the fabric with a slight pressure drop across the fabric resulting from exhaustion of gases from the upper portion of the chamber. This design forces the ammonia through a 12-inch length of the fabric while at the same time preventing escape of byproduct and unused gases into the laboratory. The module was also designed such that it might be installed as a separate stage in semi-scale finishing range for more detailed evaluation later.

Initial evaluation of the module on the "bench top" showed that fabric can be effectively ammoniated on a continuous basis. Ammonia flow rates as low as 1.0 l.p.m. and ammoniation times of 3 seconds were demonstrated to be effective for half-width cotton sateen (8.7 oz./yd.<sup>2</sup>) impregnated with 40-percent THPOH solution.

In order to demonstrate the use of forced ammoniation for insolubilization of THPOH within textile substrates, regardless of weight of construction, cotton print cloth (3.2 oz.), cotton jersey knit (4.7 and 6.9 oz.), cotton flannel-ette (4.0 oz.) and a nonwoven rayon-polyester laminate blanket padded through 40 percent aqueous THPOH and squeezed at 60 p.s.i.g. were ammoniated with fabric ammoniation times of 10 seconds. The samples were then oxidized with 0.5 percent H<sub>2</sub>O<sub>2</sub> for 10 minutes at room temperature, rinsed, and dried. Evaluation for flame retardancy using the oxygen index (OI) technique indicated that successful treatments were attained in all cases, but the blanket treatment was not fast to repeated rinsing. The forced ammoniation technique, used for all of these samples, made possible ammoniation of the knits in their tubular form, rather than splitting the knits before processing. As seen in the static substrate studies, slightly higher degree of flame retardancy is obtained for lightweight

<sup>5</sup>Drake, G. L., Jr., Beninate, J. V., Cooper, A. S., Jr., and others. A chemical drying and curing technique for imparting flame resistance to cotton. Symp. Int. Rech. Text. Cotonniere, 1st., Paris. Institut Textile de France, Boulogne-sur-Seine, PP. 721-733. 1969.

<sup>6</sup>Anonymous. Current prices of chemicals and related materials. Chem. Market. Rpt. 201(5): 22. January 31, 1972.



fabrics when they were predried before ammoniation, but the hand of the wet-ammoniated samples was superior to those of the predried samples.

*Half-width THPOH-NH<sub>3</sub> flame retardant process.* — Forced ammoniation was evaluated as an integral stage in a continuous THPOH-NH<sub>3</sub> cure process using the Ernst-Benz half-width finishing range. The process consists of one-dip-one-nip through aqueous THPOH, forced ammoniation with the experimental ammoniation module, one-dip-one-nip through aqueous H<sub>2</sub>O<sub>2</sub>, three-bath process wash by using water and finally drying with a gas-fired tenter. For this evaluation the pad bath was comprised of 40 percent THPOH in our routine formulation using Triton 770 as a wetting agent, and the fabric was squeezed with a rubber roll pair. The peroxide oxidation was with 10 percent aqueous H<sub>2</sub>O<sub>2</sub> solution stabilized with 0.5 percent sodium silicate. Because of the arrangement of equipment, it was necessary to break the process between washing and drying. In cases where the rubber-stainless roll pair was used to apply the THPOH, the fabric was padded in the laboratory and then passed through a dry pad in the continuous process.

Pad roll pressure was found to contribute significantly to the success of the flame retardant. Increasing roll pressure from 50 to 140 p.s.i.g. resulted in vastly improved flame retardancy in the finished goods. Resistance to loss of flame retardancy during laundering increased in the same order. It was also discovered that

comparable results to those obtained at 140 p.s.i.g. using the two rubber roll pair could be attained at 60 p.s.i.g., if a rubber-stainless steel roll combination is used.

The efficiency of forced ammoniation of THPOH impregnated cotton sateen was found to decrease with increased fabric speed over the 2 to 20 y.p.m. range. Corresponding decreases in resistance to loss of flame retardancy during laundering were also observed. It is felt that this sensitivity to fabric speed is related to the padding stage of the process, and further studies on this topic are in progress.

To determine the value of post-oxidation to the THPOH-NH<sub>3</sub> process, a run was made in which the peroxide was not added until half of the cloth had been treated. Results of this run indicate that in terms of fabric flammability the oxidized fabric is superior. As the unoxidized fabric becomes oxidized during laundering, however, the advantage gained from the post-oxidation becomes less.

### CONCLUSIONS

Forced ammoniation represents a potentially commercializable technique for chemically fixing THPOH flame retardant within the substrate matrix of cotton fabric. The quantity of ammonia needed for forced ammoniation on a continuous basis is considerably less than that required in diffusion ammoniation. Furthermore, forced ammoniation represents a technique which may be adapted to a continuous-feed, pollution-free gas recycle process.

## THP-AMIDE FLAME RETARDANT FOR HIGH QUALITY CHILDREN'S SLEEPWEAR

by

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(Presented by D. J. Daigle)

Research at the Southern Regional Research Laboratory showed that tris(hydroxymethyl)phosphine (THP) can be used with trimethylolmelamine (TMM) and methylolurea (MU) to impart durable flame resistance to cotton fabrics. This process consisted of padding cotton fabrics through an aqueous solution containing 1-1/2 MU, TMM, 1 percent mixed catalyst (magnesium chloride-citric acid) and 1 percent wetting agent. The process is called the THP-amide finish. Cotton sateen fabric padded with 28 percent solids solution (exclusive of wetting agent and catalyst) to a wet pickup of 90

percent and printcloth padded with 32 percent solids solutions with a wet pickup of 90 to 100 percent. This 32 percent solids consisted of 14.3 percent THP, 13.35 percent 1-1/2 MU and 4.45 percent TMM. The treated fabrics passed the AATCC vertical flame test after 50 laundering cycles. The treated fabrics also had good hand and appearance. Losses on breaking strength were approximately 10 percent and tearing strength losses were about 50 percent.

The effect of softeners, Velvetol O.E., Syl-Soft, and Triton X-400, were studied in conjunction with the THP-amide finish to

improve tear strength and possibly other fabric properties. Fabrics treated with the solution containing the Velvetol O. E. passed both the AATCC vertical flame test (hereinafter referred to as the 12-sec. test) and the Department of Commerce (DOCF3-71) vertical flame test which requires drying of the fabric (hereinafter referred to as the 3-sec. test) initially (before laundering or a 3-hour soap-soda boil). Fabrics treated with similar formulations containing the other softeners passed the 12-sec. test after a 3-hour soap-soda boil but failed the 3-sec. test initially. The sample treated with Velvetol O. E. retained the highest tearing strength but the improvement in flame retardancy and tearing strength over a similar sample treated without a softener was negligible. There was no real advantage in using any of the softeners.

Flannel was treated with a 32 percent THP-amide solution containing Velvetol O. E. and such catalysts as magnesium chloride-hexahydrate-citric acid (mixed catalyst) phosphoric acid, lactic acid, magnesium chloride-glycolic acid, zinc chloride-glycolic acid, and aluminum chlorhydrate. Fabrics treated with solutions containing phosphoric acid, lactic acid, and zinc chloride-glycolic acid as catalysts had the best overall properties. The sample treated with the solution containing  $\text{Al}(\text{OH})_5\text{Cl}$  had the best

hand but the flame retardancy was not durable to laundering.

The three best catalysts mentioned above were mixed with  $\text{Al}(\text{OH})_5\text{Cl}$  in which the percentage of each catalyst to  $\text{Al}(\text{OH})_5\text{Cl}$  was 0.9 to 0.1 percent, 0.7 to 0.3 percent, and 0.5 to 0.5 percent. The total solids content was 36 percent. Flannel treated with a THP-amide formulation containing 0.9 percent lactic acid and 0.1 percent  $\text{Al}(\text{OH})_5\text{Cl}$  passed the 12-sec. and 3-sec. tests, both initially and after a 3-hour soap-soda boil. The stiffness value for the treated fabric was 7.0 compared with 4.0 for the control and the tearing strength retained was approximately 50 percent.

Larger samples were padded with the THP-amide finish at the 36- and 34-percent solids level containing 0.9 percent lactic acid and 0.1 percent  $\text{Al}(\text{OH})_5\text{Cl}$  as the catalyst. Some formulations also contained approximately 6.8 percent ethylene glycol. This was done because ethylene glycol appears to be a stabilizing agent for THP. These samples displayed the same durable flame resistance as the smaller samples but the fabrics treated with solutions containing the ethylene glycol had higher stiffness value than those containing no glycol (20.2 to 4.5 and 62.0 to 15.5).

## FLAME AND WRINKLE RESISTANT FINISH FOR APPAREL GOODS

by

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(Presented by Darrell J. Donaldson)

Previous work at the Southern Regional Research Laboratory has shown that THPC reacts with cyanamide and urea. These finishes are not durable to boiling alkali solution. We propose to show that by adding trimethylol-methylglycoluril (TMMGU) to these formulations and in particular to the THPC-urea durability to boiling alkali solution and to repeated laundering is obtained. The new formulation provides wrinkle resistance in addition to flame retardancy.

TMMGU is prepared by adding 3 moles of formaldehyde to 1 mole of methylglycoluril suspended in water. The pH is adjusted to 8 by adding dibasic sodium phosphate. Within an hour a clear solution is obtained. This solution contains about 45 percent TMMGU.

In studies conducted with THPC-cyanamide, the sodium phosphate salts were found to

improve the efficiency of the reaction and therefore, the durability of the finish. Therefore, monobasic, dibasic and tribasic sodium phosphate were evaluated as catalysts in these formulations. A 35-percent total solids THPC-urea formulation was used. White print cloth was padded with these formulations to give about 90 percent wet pickup, dried at 85° C. and cured at 160° for 1 1/2 - 2 minutes. Fabrics treated with the dibasic and tribasic salts gave about the same strength retention, 60 percent tearing strength, and 115 percent breaking strength. Use of the monobasic phosphate as the catalyst produced fabric with the lowest strength retention, 45-percent tearing strength and 115 percent breaking strength. The fabrics treated with the formulations containing the dibasic and tribasic sodium phosphate as catalysts had about the same conditioned wrinkle recovery angles about



235°. The fabric treated with the formulation containing monobasic sodium phosphate as catalyst had about a 200° angle. The fabric treated with the formulation containing the dibasic sodium phosphate as a catalyst had the highest wet wrinkle recovery angle (200° W+F). All of the samples passed the vertical flame test (120 sec. ignition) after 50 laundry cycles and a 3-hour soap soda boil with char lengths of about 2.5-3.0 inches.

Various mole ratios of THPC to urea were evaluated in formulations containing dibasic sodium phosphate. A 1:1 mole ratio of THPC-urea did not produce the highest add-on as compared with 1:2 mole ratio of THPC-urea but only the samples treated with the 1:1 mole ratio passed the vertical flame test after a 3-hour soap soda boil or after 50-laundry cycles. Higher mole ratios of THPC-urea gave lower add-ons and little flame resistance.

The effect of TMMGU concentration on the efficiency of reaction and the physical properties of the treated fabrics was examined. A minimum of 2 percent TMMGU was found to be necessary for obtaining a durable finish. Higher concentrations increased the efficiency of the reaction but as the concentration approached 5 percent stiffness was imparted to treated fabric. After a consideration of hand of the treated fabric and efficiency of reaction, a 3-percent concentration of TMMGU in the pad bath is recommended.

Studies were made on a pilot plant scale to determine the optimum drying and curing conditions necessary for treating print cloth and sateen. These fabrics were padded through a 38-percent total solid solution containing 26.6 percent THPC, 8.4 percent cyanamide (1:1 mole ratio), 3 percent TMMGU and 3% Na<sub>2</sub>HPO<sub>4</sub>. The print cloth was dried at 85° C. in a roller dryer and cured at 160° for 1 1/2 minutes in a roller box. After process washing, the fabric had an 18 percent add-on. The treated fabric passed the vertical flame test after a 3-hour soap soda boil and 50-laundry cycles with a 3.0-3.2 inch char length. Fabrics cured at 160° for 1 minute passed the vertical flame test after 40 laundry cycles failed the test after 50 laundry cycles.

Sateen was padded with the same solution as above but dried and cured on a tenter frame. Samples dried at 85° C. for 2 minutes and cured at 170° for 1 minute passed the vertical flame test after 50 laundry cycles.

The hand of these fabrics were very good. The fabrics were white after treatment and did not yellow when subjected to chlorine bleaching. The treated fabrics retained about 115 and 60 percent of their breaking and tearing strength (a softener was not included in the formulation). The conditioned and wet wrinkle recovery angle was 235° to 240° and 220° (W+F), respectively, for the treated fabrics.

## INFLUENCE OF ION DEPOSITION, WATER HARDNESS, AND DETERGENTS ON FLAME RETARDANTS

by

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(Presented by Ralph J. Brysson)

Flame retardant garment fabrics and particularly those used in children's sleepwear must remain effectively flame retardant after repeated home launderings. Previous studies have shown that the cleansing agent (soap or detergent) used and the composition of the wash water can influence the durability of certain flame retardants. This study was undertaken to more fully investigate the effects of the variables associated with home laundering.

Each test consisted of 50 home laundry and tumble dry cycles. Commercial- and laboratory-prepared flame retardant cotton fabrics and synthetic fabrics were included. Four different cleaning agents (2 phosphate, 2 nonphosphate) and several variations in laundering techniques

were used.

The use of nonphosphate detergents (one commercial and one experimental), in most instances, resulted in a loss of flame retardancy before the last wash cycle.

All detergents caused a buildup of insoluble calcium and magnesium salts in the test fabrics. The amount of this buildup is dependent on a number of factors. Carbonate based detergents (nonphosphate) gave a greater disposition of the insoluble salts that did phosphate based detergents. The type of flame retardant used influences this buildup. Cotton fabric treated with finishes containing amide type cellulose reactive resins retained less calcium and magnesium than nonamide retardants. The amount of ion deposi-



tion is progressive with the number of wash cycles until an apparent "plateau" is reached. It is hypothesized that the ion deposition is cumulative until a level is reached where the deposition and loss due to washing are equal. This level depends on the detergent, the water hardness, the flame retardant, and possible fabric construction.

The addition of one cup (8 oz.) of common white vinegar (5 percent acetic acid) to the first rinse cycle, reduces the rate of calcium and magnesium buildup and in some instances increases the laundry durability of the flame retardant cotton fabrics.

Considerably more calcium and magnesium was retained by an untreated, fairly loose woven, cotton flannelette than was retained by an untreated barber cloth hand towel. Similar flannelette treated with a flame retardant retained less calcium and magnesium than did the untreated fabric.

The concentration of calcium and magnesium ions (water hardness) influences, to a degree, the amount of ion deposition. The initial washings were done by using New Orleans city water with hardness of about 100 p.p.m. (average 30 p.p.m. Ca and 7 p.p.m. Mg.). A home laundry system that used only deionized water was set up. The ion concentration of this water was controlled by the addition of appro-

priate amounts of calcium and/or magnesium acetate. In one wash set using approximately 150 p.p.m. calcium and 35 p.p.m. magnesium water, roughly equivalent to water of 500 p.p.m. hardness a flame retardant cotton fabric that had retained retardancy through 50-wash cycles in New Orleans water did not pass the vertical flame test after 50 cycles.

In a related test, seven knit fabrics made of synthetic fibers deemed suitable for children's sleepwear were subjected to city water laundering and testing as specified in the children's sleepwear standards (DOC-FF-3-71). A sample of woven Nomex was included. Five of the knit fabrics failed to pass the vertical flame test. The Nomex fabric and two of the knit samples retained their retardancy after the specified 50 washes. In another test using "hard" (150 p.p.m. Ca, 35 p.p.m. Mg.) water a new durable flame retardant fabric made from a polyvinyl alcohol-polyvinyl chloride fiber (Kohjin) failed after 50 wash cycles.

The preliminary studies indicate that flame retardancy durability determinations are influenced by almost every variable in the test method. A fabric can pass or fail depending on the cleansing agent used, the type of flame retardant, the composition of the wash water and possibly the fabric construction.

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Arnold, Patricia Ann, Engineering and Development Laboratory

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